THE TEXT IS
LIGHT IN
THE BOOK

TREATISE ON

GENERAL AND INDUSTRIAL

ORGANIC CHEMISTRY

GENERAL AND INDUSTRIAL ORGANIC CHEMISTRY

BY

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TRANSLATED FROM THE SECOND ENLARGED AND REVISED ITALIAN EDITION BY

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TRANSLATOR'S PREFACE

For the purposes of this English translation of his "Trattata di Chimica Organica," the author has made a number of alterations in and additions to the text of the second Italian edition, these consisting principally in amplifications of the statistical data referring to Great Britain and the United States.

It has been deemed undesirable to convert the metric weights and measures into those of the English system, but, in general, prices are given in British currency, twenty-five lire being taken as the equivalent of one pound sterling. Where quantities are given in tons, the latter are to be read as metric tons of 1000 kilograms or 2204·6 lb. avoirdupois.

The abbreviations employed for the different units of weights and measures are those in common use, and temperatures are expressed in degrees Centigrade in all cases.

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PREFACE TO THE SECOND ITALIAN EDITION

THE first edition of this treatise on Organic Chemistry was published in two volumes in 1908 and 1909, and rapidly exhausted, the second edition being now published in one volume. The distribution of the matter is similar to that of the first edition, but many chapters have been brought up to date, others have been considerably amplified and others again have been introduced for the first time. The largest additions have been made in the chapters dealing with the treatment of tar, with colouring-matters, with alkaloids, &c.

The statistics of production, exportation, and importation have been brought up to the year 1910 and, where possible, to 1911. Special attention has been devoted to this characteristic feature of the book, as experience has shown the author that among the most important factors in deciding the possibility or convenience of starting new or of extending existing industries are those governed by the laws of economics and statistics.

The author will be grateful to any readers or colleagues who may point out omissions or errors, which are unavoidable in a work of this character with such varied contents in so condensed a form.

This second edition is in course of translation into English and German.

E. MOLINARI

MILAN

PREFACE TO THE FIRST ITALIAN EDITION

A NEW treatise on Organic Chemistry might, in view of the existence of the excellent works of Bernthsen and Holleman, be considered superfluous.

But both of these books, which differ little in the manner in which the subject is developed, are confined to a theoretical and systematic exposition of the many organic compounds, the industrial side of the question and the applications of these compounds being almost entirely neglected. It is hence difficult for the student to ascertain which of the thousands of substances described are really of practical importance.

Modern teaching of chemistry adheres in a too one-sided manner to the old but fruitful idea of Liebig, that "to obtain a sound practical man it is necessary to train a good theorist." This conception was taken too literally, although it gave good results when chemical industry was in its infancy, since in those days any theorist could easily introduce new and important methods. But to-day, when the industry has attained the adult stage—has advanced to such an extent and become so varied and complex, being stimulated incessantly by keen national and international competition, which demands rapid changes and improvements—the valuable time of the young technician cannot be wasted in a protracted and sometimes sterile apprenticeship. Present-day conditions require, therefore, some such expansion of Liebig's maxim as the following. In order to produce, rapidly and with increased certainty, a sound, practical man, it is necessary to train a good theorist and to initiate him into both the theoretical and practical study of the more salient industrial problems.

It does not suffice that the young chemist, about to begin his industrial or teaching career, should have a thorough knowledge, for instance, of the various syntheses and constitutional formulæ of the sugars. He should also be acquainted with at least the general outlines of the industrial processes and of the technique of the manufacture of sugar, beginning with the slicing of the beets and proceeding to the exhaustion of the pulp, defecation, saturation, filtration with filter-presses, boiling, and vacuum concentration in multiple-effect apparatus, refining and centrifugation of sugar crystals, utilisation of residues, and so on. He should, indeed, understand the plant and chemical processes of the more important industries, as these often find application in the manufacture of products of a secondary or entirely new character.

What would avail a study of the wonderful artificial colouring-matters derived from coal-tar, with the inexhaustible syntheses composing their theoretical basis, if it were limited to a simple mnemonic exercise for the student and no notice were taken of the interesting practical applications to the dyeing of the various textile fibres?

Nor should the young student ignore statistics of production; he should be able to appreciate the importance of variations in the exportation and importation of the principal chemical products, and to judge of the economic and social conditions with which such variations correspond.

After a brief novitiate, he should be in a position to point out the more striking technical defects and the more marked difficulties met with in particular industrial processes and to suggest rational and not fanciful remedies

It is this space, the vacant region representing a suitable fusion of theoretical with applied chemistry, which requires filling. This I have attempted in the present work, which of itself is certainly insufficient to cover the whole of the ground.

The difficulties encountered in preparing the volume on Inorganic Chemistry are multiplied in dealing with Organic Chemistry, and this is the case not only as regards the collection and confirmation of the statistical data but of the chemical processes giving the best results in practice. For in any particular industry it has often been found that the results of investigations are in such disaccord with the practical data as to render it a matter of great uncertainty what conclusions should be presented to the reader.

Inquiries addressed to manufacturers resulted in aggravation of this uncertainty, what was confirmed on the one hand being denied on the other, and plant guaranteed by one firm to be the best being decried by a competing firm. It hence became necessary to apply directly to the operatives working a given process and to draw conclusions from the whole of the data and information thus obtained.

It is thus that readers may explain the contradictions between different authorities on one and the same subject, and also the fact that the conclusions reached by the author with reference to certain industrial processes are not always in accord with those given in other treatises.

The intention has certainly not been to prepare a complete treatise on technological chemistry and still less on chemical technology. The work having to be restricted within limits of space approximating to those of vol. i, the author has descended to details only with some of the principal industries and especially with those best adapted to give a general idea of the different applications of chemical processes and of chemical technics.

To this end the author has dwelt preferably on the industries of illuminating gas, sugar, alcohol, beer, acetic acid, dyeing, textile fibres, fats and soaps, explosives, &c.

From these examples the student may gather much instruction applicable to many other industries not dealt with in detail.

Repetition has been avoided and time and space saved by frequent references to arguments already developed in vol. i, "Inorganic Chemistry."

Advice and collaboration are desired from readers and colleagues in order that gaps in the present work may be filled and inaccuracies and defects remedied.

E. MOLINARI

MILAN

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BB. HALOGEN DERIVATIVES OF HYDROCARBONS

CC. ALCOHOLS

EE. ACIDS

ERRATUM

Page 386, line 28, *for* gallatite *read* gallalith

PART I. GENERAL

In vol. i of this treatise[1] is given a brief summary of the history of chemistry and of those portions of physico-chemical theory which are necessary for the interpretation of chemical phenomena.

Hence, this course of organic chemistry assumes in the reader a knowledge of the fundamental chemical laws and ideas, methods of determining molecular weights, and so on.

The separate treatment of the carbon compounds, which is termed *organic chemistry*, is a purely didactic convenience and somewhat of a habit, there being no sound foundation to justify a distinction between organic and inorganic chemistry.

This division of the subject dates back to the time of Lemery, who, in 1675, regarded the substances of the animal and vegetable kingdoms as distinct from those of the mineral kingdom, and to 1820, when Berzelius justified the separation by stating that the preparation of organic compounds required the intervention of *vital force*, whilst inorganic compounds could be prepared artificially in the laboratory. But this view was abandoned in 1828, when *Wohler* succeeded in preparing *urea* (found in urine) from inorganic material in the laboratory, and, later, when acetic acid was prepared artificially. Subsequently, the number of so-called organic compounds which have been obtained synthetically has increased almost without limit.

There exists to-day no reason for a distinction between organic and inorganic compounds; the first comprise a group of carbon compounds embracing an immense number (over 150,000) of substances, which exhibit certain common characters and are conveniently studied by themselves.

It had already been recognised by Lavoisier that all so-called *organic* compounds, originating in *organised* bodies, contain *carbon*, *hydrogen*, and *oxygen*, and that many of them, especially those of the animal kingdom, contain also *nitrogen* and sometimes *sulphur*, *phosphorus*, *halogens*, and *metals*.

The study of organic compounds is as old as the human race, which, from the most remote times, has prepared alcohol and acetic acid from vegetable juices (the must of the grape and other fruit, &c.).

After the discoveries of Lavoisier and the investigations of Berzelius, organic chemistry began to acquire a special importance. And Liebig, by introducing simple and exact methods for the analysis of organic compounds, rendered most valuable help to the wonderful theoretical and practical development which has been shown by this branch of chemistry during the past fifty years, and which has been largely responsible for the impulse given to progress and civilisation in the nineteenth century.

In order to study the innumerable derivatives of carbon, to be able to obtain separate individuals and to characterise them by means of their chemical and physical properties, then to group and classify them and to deduce in a more or less general way the laws they obey, it was necessary to isolate and prepare in the *pure* state these separate chemical individuals.

[1] E. Molinari, "Inorganic Chemistry"; Translated by E. Feilmann, 1912.

PURIFICATION OF ORGANIC SUBSTANCES

The purification of organic substances is not so easy to effect as might appear at first sight. Pure substances are characterised by certain physical constants (boiling-point, melting-point, crystalline form, &c.), which serve to show if a substance is in a suitable condition for chemical analysis.

The chemical processes of *purification* may be deduced from the chemical properties of the substances themselves, as described in Parts II and III of this treatise; general physical methods effect *purification by means of suitable solvents* (water, alcohol, ether, light petroleum, acetic acid, benzene, acetone, chloroform, carbon disulphide, &c.), which separate certain substances from others more or less soluble; or, in many cases, purification is brought about by *crystallisation,* a solution of the impure substance in a suitable hot solvent depositing—on gradual cooling or partial evaporation of the solvent—the pure substance in characteristic and well-defined crystalline forms, which can be controlled by measuring the angles and determining the axial ratios of the crystals.

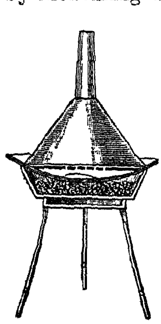


FIG 1

Impurities separate sometimes before and sometimes after the crystallisation of the substance under examination, so that recourse is had to *fractional crystallisation,* which, when repeated, may give excellent results.

In certain cases, substances are purified by *sublimation.*[1] When pure, a liquid has a constant *boiling-point* for a definite pressure (vol. i. p. 81), and this is determined by *distilling* the liquid in a flask with a lateral tube, a thermometer being arranged in the neck of the flask without its bulb dipping into the boiling liquid. The temperature of the vapour gives the boiling-point of the liquid; the vapour escapes from the side-tube and is condensed by means of a *Liebig's condenser,* formed of an inclined glass tube surrounded by a wider tube through which water circulates from the lower to the upper end (Fig. 2).

The boiling-point of a very small quantity of substance can be accurately determined by means of the arrangement shown in Fig. 3: a few drops of the liquid are introduced into a small tube, *d,* closed at the bottom and drawn out into a narrowed part. Into the liquid dips a capillary tube, sealed at the point *a* by fusing the glass. The tube is attached to the thermometer, *c,* and the whole immersed, to the depth of a few centimetres, in a liquid having a boiling-point higher than that of the liquid under examination. Heat is now gradually applied, superheating being prevented by the air-bubbles issuing from the lower end of the capillary tube. When the boiling-point is reached, bubbles form very rapidly at the bottom of the liquid, and the boiling-point is read off on the thermometer.

Certain substances which readily decompose on boiling at the ordinary pressure can be distilled unchanged at a constant, but somewhat lower, temperature by lowering the pressure, *i.e.* by distilling in a vacuum (*see later*). For this purpose use is made of a mercury or water pump (Sprengel).

When two liquids are mixed, they can be separated almost completely by *fractional distillation,* if there is a wide interval of temperature between their boiling-points. In consequence of the partial pressure of the components, at different temperatures mixtures distil over which contain varying proportions of these components; the liquid with the lower boiling-point first preponderates in the distillate, while at higher temperatures that with the higher boiling-point preponderates. On repeated redistillation of the two extreme fractions separately, the two liquids can be obtained in the pure state. In certain cases, however, a mixture of two liquids does not exhibit a regular progression in the vapour pressure corresponding with the preponderance of one or other of the two components. There are, indeed, liquids which, when mixed in certain proportions, show a minimum vapour pressure—lower even than that of the less volatile component—whilst,

[1] *Sublimation* takes place with many solid substances and consists in the passage from solid to vapour on gentle heating, and from the state of vapour to the solid crystalline condition when the vapours come into contact with a cold body. these changes taking place directly and not by way of the liquid state. Usually the substance is placed on a clock-glass, covered by a perforated filter-paper and by a funnel; on heating the clock-glass on a sand-bath, the pure sublimed crystals collect on the walls of the funnel (Fig. 1). In some cases, the sublimation is carried out in a vacuum.

on the other hand, a mixture of two liquids sometimes has a vapour pressure greater than that of its more volatile constituent; the two liquids cannot then be separated by fractional distillation, especially when their boiling-points are not far apart.[1] In these cases good results are obtained practically by employing so-called *rectification*, this consisting in distilling the liquid mixture through a Le Bel and Henninger (1874) rectifying tube

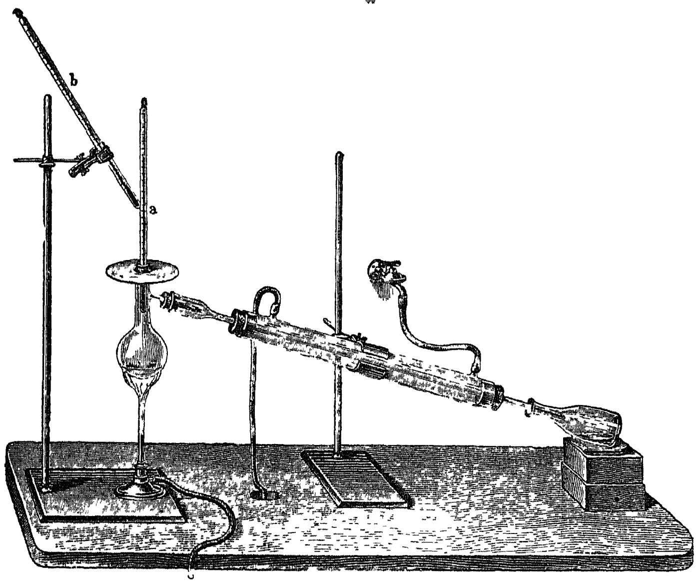


FIG. 2.

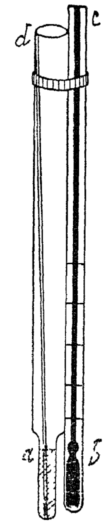


FIG. 3.

(Fig. 4), which is fitted at regular intervals with discs of platinum gauze, and above these takes the form of a series of two or more bulbs, a lateral tube being so placed as to lead the liquid condensing in any bulb back to the bulb below it. When the liquid boils, the mixed vapours pass up the tube and meet the first gauze disc, where the vapour of the less volatile liquid is condensed in greater proportion than the other, so that the vapour reaching the second gauze is richer in that of the more volatile liquid; a similar process occurs at the successive gauzes and in the bulbs above them, so that the vapour passing through the uppermost bulb is that of the more volatile liquid, and this passes down the side-tube (at the mouth of which the thermometer is placed) to the condenser. During this rectification the cooling produced by the outer air and the consequent condensation of the vapours result, in the rectifying tube, in a stream of liquid flowing down the walls of the tube; this liquid meets the ascending vapours and gives up to them its more volatile constituent and takes up from them their less volatile component, so that only the vapour of the more volatile liquid reaches the top of the tube, while the less volatile liquid is returned.

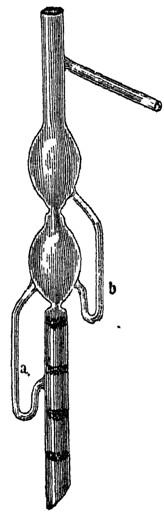


FIG. 4.

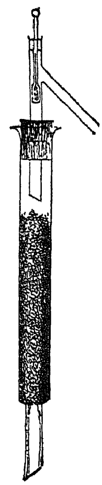


FIG. 5.

Similar results are obtained by *Hempel's rectifying column* (1881), which is filled with glass beads (Fig. 5). With this also the phenomenon of rectification which goes on often

[1] *Theory of Fractional Distillation.* We shall see later the relations existing between the boiling-point and the composition and chemical constitution of organic substances (homologous series, isomerides, &c.). Of interest at the present juncture is the behaviour on distillation of a mixture of two liquids which dissolve one in the other in all proportions.

According to Wanklyn and Berthelot, when a mixture of equal weights of two liquids is distilled, the proportions of the two in the distillate depend not only on their proportions in the original liquid and on their vapour pressures at the boiling-point of the mixture itself, but also on the reciprocal adhesion of the constituent liquids

permits of the separation of liquids with boiling-points quite close together. This phenomenon has important applications in the alcohol industry (*see later*), in the manufacture of oxygen and nitrogen from *liquid air*, in the preparation of liquid sulphur dioxide (vol. i, pp. 245 and 295), and in many other industries.

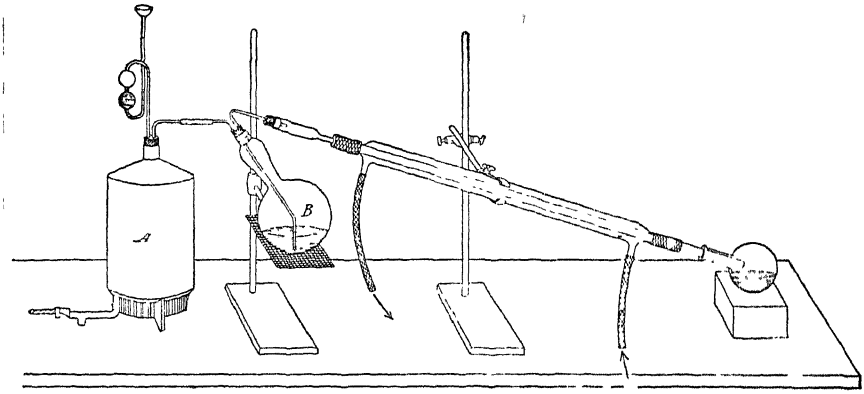


FIG. 6.

In many cases substances (liquid or solid) are purified by distilling in a current of steam, certain of them being volatile under these conditions even when their boiling-points are above that of water ; in the distillate the substance often separates owing to its insolubility in water. An arrangement used in the laboratory is shown in Fig. 6, steam being generated in *A* and passing through the substance to be distilled in the flask, *B*, which can be heated directly with a flame.

In some instances the distillation is effected by means of *superheated steam* (150°–350°), which is obtained by passing steam through a coil of iron or copper tubing heated with a bunsen burner (Fig. 7).

A number of substances decompose when heated at the ordinary pressure, whilst they

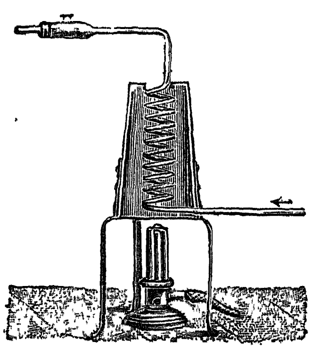


FIG. 7.

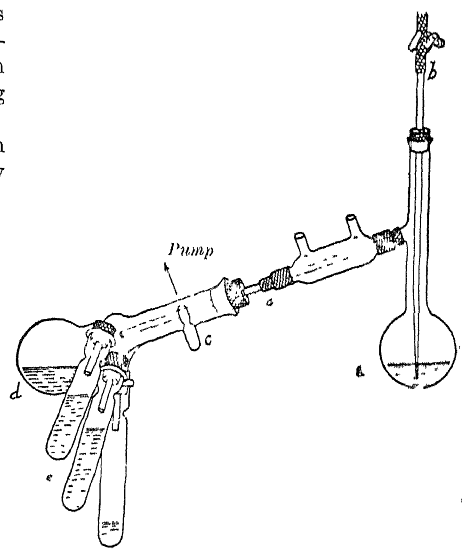


FIG. 8.

distil unchanged in a more or less perfect vacuum, owing to a marked lowering of the boiling-point. Of the many different forms of apparatus employed in the laboratory for

and on their *vapour densities*. When a mixture of two miscible liquids, in equal weights, is distilled, the quantity of each component which distils can (disregarding certain exceptions) be calculated by multiplying the vapour pressure (at the boiling-point of the mixture) by the vapour density. Hence it can be understood how, in some cases, the less volatile substance distils in greater quantity. Even if the vapours that distil over contain equal volumes of the two vapours (that is, equal numbers of molecules), the condensed liquid will contain a greater proportion by weight of the constituent with the higher molecular weight This explains why water, with a low vapour density, causes substances with higher boiling-points (ethereal oils, naphthalene, &c.) to distil, since, although the latter have low vapour pressures, their molecular weights are high.

On distilling a mixture of two liquids not soluble one in the other, the corresponding vapours do not influence

this purpose, that of Bredt is illustrated in Fig. 8. An ordinary thick-walled distilling flask, *A*, is used, its side-tube being connected with the condenser *a* and with the collecting apparatus, which consists of a flask, *d*, and three tubes, *e*, of thick glass, and is joined to the condenser by means of a perforated stopper; the pump by which the air is withdrawn from the whole apparatus is connected with the tube, *c*, which communicates also with a manometer to show the extent of the vacuum attained. Superheating and consequent bumping of the liquid are avoided by the insertion of the tube *b*, the lower end of which is drawn out to a capillary and dips below the surface of the liquid, while the upper end is closed with a piece of rubber tubing fitted with a screw-clip; by means of this tube, into which also the thermometer may be introduced, a slow current of air or other inert gas, controlled by means of the screw-clip, is allowed to bubble through the liquid. The flask is heated in a bath of oil or fusible alloy, and, if the distillate is very dense, no water need be passed through the condenser. The first portion distilling over at a definite temperature is collected in *d*, and when the temperature rises suddenly, the collecting apparatus is rotated so that the distillate is collected in one of the tubes, *e*; when the thermometer no longer indicates a constant temperature, another of the tubes, *e*, is employed, and so on.

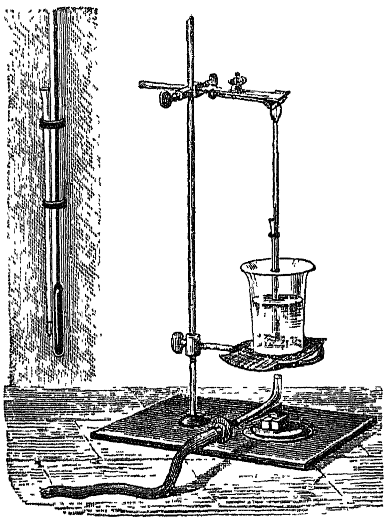


FIG. 9.

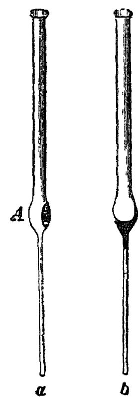


FIG. 10.

MELTING-POINTS. Whilst with liquids the boiling-point is generally used as a criterion of purity, for solids the melting-point is mostly employed for this purpose, and in certain cases also the boiling-point. So long as the substance is impure, the melting-point is usually too low. The melting-point is determined by introducing a few centigrams of the substance into a very narrow, almost capillary glass tube closed at the bottom (Fig. 9), the tube being attached to the bulb of a thermometer dipping into a beaker of concentrated sulphuric acid, oil, or paraffin, which serves to transmit heat to the substance. A small glass stirrer serves to prevent superheating of the liquid, and, when the substance is pure, it melts entirely within a degree and generally becomes transparent. When the temperature of the bath approaches the melting-point the flame is lowered and the bath heated gently so that the temperature rises half a degree every four or five seconds; only in exceptional cases should rapid heating be continued.

To determine the melting-point of a fat, a tube drawn out to a capillary and sealed at the lower end (Fig. 10*a*) is held in an inclined position, and one or two drops of the fused and filtered fat introduced into the enlarged part (*A*, Fig. 10*a*). When the fat is solidified, the tube is kept in a cool place for twenty-four hours, after which it is attached vertically to the bulb of a thermometer; it is then heated in a suitable bath, note being taken of the temperature at which (1) fusion begins, (2) the fat flows down and obstructs the capillary (Fig. 10*b*), and (3) the completion of fusion is indicated by the entire liquefaction and transparency of the fat.

one another, and the total pressure of the vapours is given by the sum of the pressures of the two liquids at the temperature of distillation. The boiling-point of the mixture is the temperature at which the sum of the vapour pressures of the components equals the atmospheric pressure; it should be mentioned that the boiling-point of such a mixture is necessarily lower than that of the more volatile liquid, since here also *Dalton's law of partial pressures* (vol. i, pp. 71, 383, 491) holds. Naumann (1877) showed that, in the vapour distilling from such a mixture the ratio between the volumes of the components corresponds with the ratio between the vapour pressures of the two liquids at the boiling-point of the mixture; and hence the *weights* of the two components are obtained by multiplying these ratios by the corresponding densities (or molecular weights). By means of this rule, Naumann succeeded in determining the molecular weights of various substances simply by distilling mixtures of them. A mixture of water and isoamyl alcohol (b.pt. 135°) has a constant boiling-point of 96°, and distils continuously in the ratio of two volumes of water and three volumes of the alcohol.

The melting-point of a fat can also be determined by drawing it in the fused condition into a capillary tube blown out at the middle into a bulb, which is half filled with the fat (Fig. 11); the upper end of the tube is kept closed with the finger until the fat becomes solid, the empty part of the tube being then bent round as shown and attached, upside down, to a thermometer, the whole being afterwards gradually heated in a beaker of water. When the fat begins to melt it flows into the lower part of the bulb (Fig. 11 *A b*, right-hand view), and when it is completely fused it becomes transparent.

For fats and paraffins, or waxes in general, and for *soft fats* (for example, lubricants) especially, an important determination is that of the *dropping-point*, which is carried out, according to Ubbelohde's method (1905), by filling with the fat a glass capsule, *e* (Fig. 12, natural size), 10 mm. long and 7 mm. wide, with an orifice 3 mm. in diameter in the base; a very small thermometer bulb is immersed in the fat and the capsule then affixed to the thermometer with a metal sheath having an aperature at *c*, and three points, *d*, which determine the position of the capsule; the thermometer is then fixed in a test-tube 4 cm. in diameter, dipping into a beaker of water, which is heated so that the temperature rises one degree per minute. At the orifice of the capsule a drop begins to form at a certain time, and when this falls the temperature is read, and is usually corrected by subtracting 0·5 to obtain the *real* instead of the apparent dropping-point.

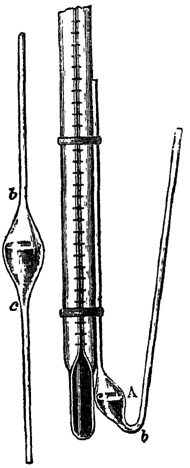


FIG. 11.

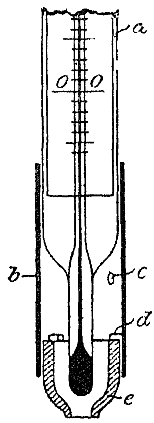


FIG. 12.

This method has been adopted for the examination of lubricating oils supplied to the Italian navy and railways.

The **specific gravity** of liquids also serves to determine their purity, and the various forms of apparatus used for measuring it are described in vol. I, p. 72.

ANALYSIS OF ORGANIC SUBSTANCES

As will be seen later, many so-called organic substances are composed of carbon and hydrogen combined in various proportions; a large number of them also contain oxygen, while nitrogen is often present and sometimes sulphur, halogens, metalloids, and metals.

Analysis of these compounds may be merely *qualitative*, when only a knowledge of the constituent elements is required, or it may be *quantitative* when the percentage amount of each of the elements present is determined.

QUALITATIVE COMPOSITION. When organic substances are heated on platinum foil they either burn with a flame or leave a carbonaceous residue. The presence of *carbon* and *hydrogen* may be demonstrated by heating a little of the substance, mixed with cupric oxide, in a test-tube fitted with a delivery tube, the gas evolved being passed into a clear solution of barium hydroxide: if the latter becomes turbid, owing to the formation of barium carbonate, the presence of carbon is proved, and if drops of water condense in the cold upper part of the tube the substance must contain hydrogen.

The presence of *nitrogen* can, in many cases, be shown by the smell of burning wool or nails developed when a little of the substance is heated on platinum foil. A more general and certain test is that devised by Lassaigne (1843): 2–3 centigrams of the substance are fused with a piece of metallic potassium or sodium (0·2–0·3 grm.) in a test-tube, which is broken by plunging it while still hot into a beaker containing 10–12 c.c. of water. The alkaline solution of potassium cyanide formed is filtered, mixed with a few drops of ferrous sulphate and ferric chloride solutions and boiled for two minutes, by which means potassium ferrous cyanide is formed (when nitrogen is present in the substance); the liquid is acidified with hydrochloric acid, which dissolves the ferrous and ferric oxides,

the resulting ferric chloride reacting with the potassium ferrocyanide to form the characteristic Prussian blue, or at least a green solution which deposits Prussian blue on standing. In absence of nitrogen, only a yellow colour is obtained. To certain nitrogenous substances this test is not applicable (*e.g.* to diazo-compounds, which evolve nitrogen too readily), and in such cases either the potassium is replaced by a mixture of potassium carbonate and powdered magnesium (Castellana, 1904), or the substance is fused with sodium peroxide and the mass tested for nitrate by means of diphenylamine (vol. i, p. 214).

The presence of *halogens* (Cl, Br, I) is determined by heating the substance with *pure* lime, dissolving in water and nitric acid and precipitating the halogen with silver nitrate. Also, in many cases, the substance can be heated with fuming nitric acid and silver nitrate in a sealed tube (*see later*, Quantitative Analysis), by which means the silver halogen salt is formed directly (Carius).

Sulphur also can be detected by the Carius method, the substance being heated in a sealed tube with fuming nitric acid and the sulphuric acid, formed from the sulphur of the organic compound, precipitated with barium chloride ; or by heating the substance with pure sodium peroxide, a sulphate is formed. By heating the substance in a test-tube with metallic sodium and dissolving the mass in a little water a solution of sodium sulphide is obtained which blackens a piece of silver foil or a silver coin.

Phosphorus and other elements are detected by the Carius method, the substance being oxidised with fuming nitric acid and the liquid tested for the corresponding acid (phosphoric, &c.)

QUANTITATIVE COMPOSITION (ELEMENTARY ANALYSIS). Lavoisier first of all devised an apparatus for analysing organic substances by burning them with oxygen

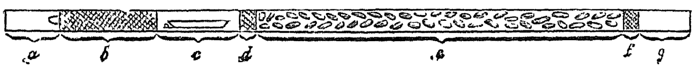


FIG. 13.

a = 5 cm. free ; b = 12 cm. spiral of oxidised copper gauze ; c = 8–10 cm for the boat ; d = 3 cm. copper spiral ; e = 40–45 cm. granulated cupric oxide ; f = 3 cm. oxidised copper spiral or 12 cm. of reduced copper spiral for nitrogenous substances ; g = 5 cm. free.

under a bell-jar ; while Gay-Lussac, Thénard, and Berzelius successively improved this process by burning the substance in presence of potassium chlorate. Gay-Lussac, however, showed that certain nitrogenous substances cannot be burned with the chlorate, and suggested as a general and more certain oxidising agent cupric oxide, which when hot gives up its oxygen, transforming the carbon and hydrogen of any organic compound into carbon dioxide and water respectively, while the nitrous compounds are reduced to free nitrogen by passing the products of combustion over red-hot copper turnings. But it is to Liebig that the credit is due of rendering this method of organic analysis simple and exact and of devising simple and ingenious forms of apparatus for absorbing the products of combustion. Even to-day—disregarding improvements in combustion furnaces and modifications of the absorption apparatus—the **determination of carbon and hydrogen** (the oxygen is estimated by difference) is carried out by what is virtually the method employed by Liebig.

The method most commonly used is as follows : 0·15–0·30 grm. of the substance is weighed in a small porcelain boat, which is then filled with powdered cupric oxide, previously heated to redness and *perfectly dry ;* the boat is then introduced into the position c of the hard glass combustion tube (Fig. 13), this being 70–90 cm. long, or 10–12 cm. longer than the combustion furnace, which is heated by 25–30 gas flames (Fig. 14).

The other parts of the tube are reserved for the previously heated copper spirals and granulated cupric oxide (Fig. 13). When a fresh combustion is to be made, all that it is necessary to do is to remove the spiral b and the boat and to introduce the new substance into the tube, which is already charged in d, e, and f and is not allowed to cool below 40°–60°.

The combustion is carried out in the furnace shown in Fig. 14, the tube being closed at a with a good cork and a glass tap which can be connected at will with a gasometer containing air or one containing oxygen, which should, however, before reaching the combustion tube, pass through tubes containing potassium hydroxide to remove the

carbon dioxide, and then through drying tubes containing calcium chloride. At the other end the combustion tube communicates at *b*, first with a tared tube, *c*, containing granulated calcium chloride to absorb the water formed during combustion; then follows the tared apparatus *d*, containing potassium hydroxide solution (30–35 per cent.), which absorbs the carbon dioxide from the burnt substance and is furnished with a calcium chloride tube to retain the moisture given off by the potassium hydroxide solution. Finally follows a calcium chloride tube, *e*, which is not weighed and prevents moisture entering the apparatus from the air.

Before the combustion is started the apparatus is tested to ascertain if it is perfectly air-tight. This is done by closing the tap *a*, and sucking into *e* eight or ten bubbles of gas; the slight rarefaction produced in the interior of the combustion tube causes the potash solution to rise in the first large bulb to a level which should remain constant for some minutes. The burners at the end *b* are then gradually lighted until the portion *f* and almost all of the portion *e* are heated to redness. The spiral *b* is then gradually heated from the *a* end, the heating being gradually extended under the boat so that the substance is completely burnt. During the combustion bubbles of air are passed into the tube from the gas-holder so as to transport the gases produced into the absorption apparatus; during the last 10–15 minutes a gentle current of oxygen is passed through, and then the flames are extinguished and air again passed for 10–15 minutes. In this way all the gases from the combustion are removed from the combustion apparatus and the copper oxide is completely reoxidised, so that the tube is ready for the next combustion.

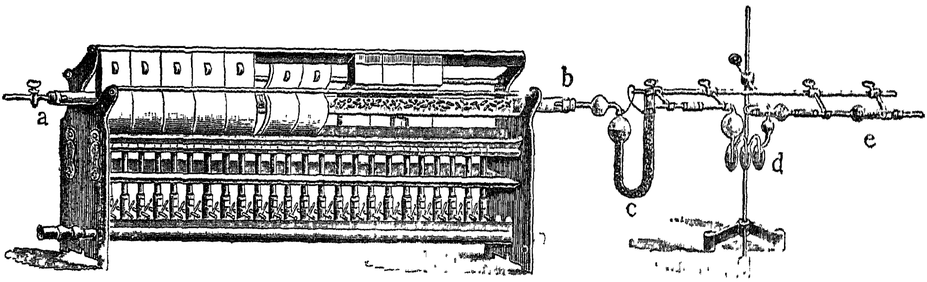


FIG. 14.

The increases in the weights of the potash and calcium chloride apparatus give the amounts of carbon dioxide and water respectively formed during the combustion, and, since 44 parts of carbon dioxide correspond with 12 parts of carbon and 18 parts of water with 2 of hydrogen, the quantities or percentages of carbon and hydrogen in the substance can be calculated. The sum of these two percentages, when subtracted from 100, gives that of the oxygen, excepting where the substance contains nitrogen, which is determined directly by methods given later. In this way the *percentage composition* is determined.

For determining carbon and hydrogen in *nitrogenous substances* the above method is modified only by inserting in the combustion tube, in place of the spiral *f* (Fig. 13), one of reduced copper gauze[1] about 15 cm. long, this serving to fix the oxygen from the oxides of nitrogen resulting from the combustion and to liberate the nitrogen, which passes unchanged through the absorption apparatus.

If the substance to be analysed contains *sulphur* or a *halogen*, the combustion is made with lead chromate in place of the granular copper oxide, and the heating is more gentle to avoid fusion of the chromate. By this means the sulphur remains fixed in the tube as lead sulphate and the halogens as halogen salts of lead. Halogens can also be fixed on a spiral of silver foil about 10 cm. long placed at *f* (Fig. 13), the substance being combusted as usual with cupric oxide; if both nitrogen and a halogen are present the copper and silver spirals are used together.

A new apparatus, which admits of the combustion of organic substances being very rapidly carried out, is that devised by Carrasco and Plancher (1904–1906). It consists of

[1] The reduction is effected in a separate glass tube, through which a current of hydrogen is passed while the spirals are heated; when the copper has assumed its characteristic red colour, the flames are extinguished and the spirals allowed to cool in the current of hydrogen, being afterwards kept in desiccators ready for use; or, better, when reduction is complete and the spirals are still hot, the tube is exhausted and is kept so until cold, so as to avoid the danger of hydrogen being occluded by the copper.

a small external combustion tube, *c* (Fig. 15), of hard glass and about 20 cm. long and 2 cm. wide and slightly expanded at the lower closed end. The tube is closed at the top by a rubber stopper, *f*, through which passes a porcelain tube, *e*, wound round with an electric resistance formed of platinum-iridium wire, *d*; along the interior of the porcelain tubes passes a thick silver wire, which starts from *d*, the negative pole, and ends in a small platinum wire loop and serves to convey the current (3 amps. at 20 volts). The oxygen for the combustion traverses *OS* and the upright tube of the stand, and passes through the porcelain tube to the bottom of the combustion tube. In the stopper, *f*, is fastened a piece of nickel tube, *b*, which is united to the + pole and to the platinum spiral, *d*, and serves at the same time for the escape of the gases formed by the combustion to the tube *r*. The gases are absorbed by the usual tared apparatus (*u*=calcium chloride,

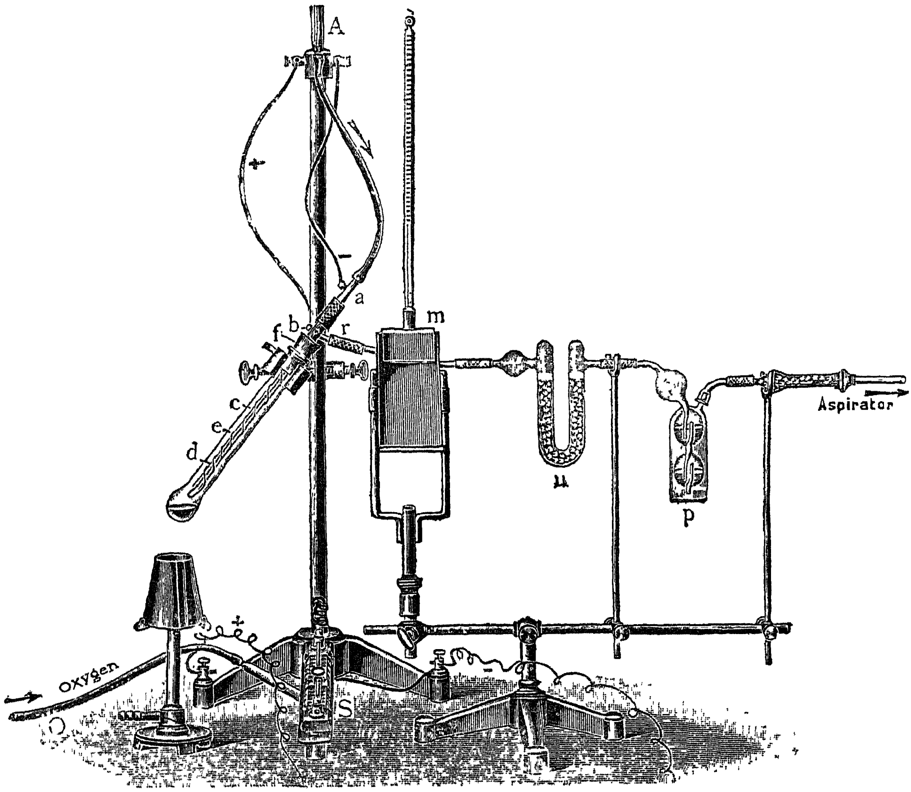


FIG. 15.

p=concentrated potassium hydroxide solution), but with nitrogenous or halogenated substances the gases are first passed through a U-tube containing lead dioxide heated to 180° by means of a small furnace, *m*. The connections *a* and *b* are insulated from one another by porcelain and rubber. When the current passes through the resistance the glass tube is heated to redness, and the substance (0·12–0·20 grm.), mixed with cupric oxide or, better, with platinised porous porcelain powder, and placed at the bottom of the glass tube, is burned by heating the outside of the tube directly with a Bunsen flame. The combustion is very soon completed, the platinum-iridium spiral apparently accelerating the oxidation catalytically; apart from the time occupied by the weighings, this method requires 15–20 minutes, and usually gives good results. For the analysis of fairly volatile liquids or of substances which readily sublime, the lower part of the combustion tube is drawn out almost horizontally, and the substance is mixed with platinised porcelain powder (2–3 per cent. of platinum); liquids can be heated in a separate tube and the vapour then injected into the combustion tube.

An electrical method for determining carbon, hydrogen, and sulphur in organic subtances was also proposed by Morse and Gray in America in 1906.

QUANTITATIVE DETERMINATION OF NITROGEN. (1) *Dumas' Method.* The nitrogenous organic substance (0·2–0·3 grm.) is heated in a hard glass tube similar to that shown in Fig. 13, but closed at the end, *a*. The portions *a* and *b* contain sodium hydrogen carbonate or magnesium carbonate; between *b* and *c* is placed a small plug of copper gauze, in *c* granulated copper oxide, and in *d* powdered copper oxide. Then follows a space 10 cm. in length in which is placed the substance to be analysed, this being weighed and mixed with powdered cupric oxide; next comes granulated cupric oxide, and in *f* a spiral of reduced copper, 10–12 cm. long.[1]

The extremity, *g*, of the tube is connected by means of a gas delivery tube with a graduated tube (25 or 50 c.c.), placed upside down in a basin of mercury and filled half with mercury and half with concentrated potassium hydroxide solution. This graduated tube may have the form devised by Dumas and shown in Fig. 16; the gas from the combustion tube passes into the tube *a*, furnished with a clip, *m*, thence through a little mercury in the bottom of the tube *b*, which is filled with potassium hydroxide solution and is in communication with a reservoir, *c*, of this solution. The operation is begun by heating the combustion tube at the point where the magnesium carbonate lies; the carbon dioxide thus evolved expels the air from the apparatus into *b*, whence it is driven by raising the reservoir, *c*, and opening the cock at the top of *b*. The carbon dioxide is absorbed by the potash solution, and when no more air collects in *b* the magnesium carbonate is no longer heated. The copper spiral and the copper oxide are now gradually heated in the same way as for the estimation of carbon and hydrogen, the heating being slowly extended until it reaches the substance itself. Oxides of nitrogen are decomposed by the copper spiral, so that all the nitrogen is evolved in the free state and collects in *b*. Finally the nitrogen remaining in the combustion tube is driven into *b* by means of carbon dioxide formed by again heating the magnesium carbonate.

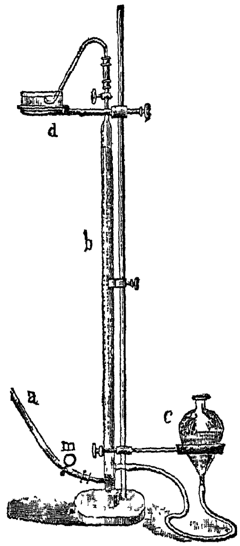


FIG. 16.

At the end of the operation, in order to measure the nitrogen, a graduated tube filled with water is inverted over *d*, and the cock at the top of *b* having been opened, the reservoir, *c*, is raised until all the gas passes into the graduated tube. The latter can then be removed to a large cylinder full of water and when, after a few minutes, the gas has assumed the temperature of the water (shown by an accurate thermometer) the tube, grasped by a clip (the hand would warm it), is arranged so that the level of the liquid inside it coincides with that outside and the volume (v) of the gas read off. At the same time the atmospheric pressure (b) is read, and the exact temperature (t) of the water. The percentage of nitrogen (p) in the substance is then calculated by means of the following formula:

$$p = \frac{v\,.\,(b - w)\,.\,0{\cdot}12511}{s\,.\,760(1 + 0{\cdot}00367\,.\,t)}$$

where s indicates the weight of substance taken, w the pressure of water vapour expressed in mm. of mercury (*see* vol. i. p. 34) and 0·0012511 grm. the weight of 1 c.c. of moist nitrogen at 0° and 760 mm. (Rayleigh and Ramsay).

When several determinations of nitrogen are to be carried out the procedure is sometimes simplified by using a combustion tube open at both ends, like that of Fig. 13, the magnesium carbonate or sodium bicarbonate being omitted and the combustion tube being connected at *a* with a small Kipp's apparatus for the evolution of carbon dioxide (marble and hydrochloric acid), care being taken to free the apparatus from all air by a prolonged current of carbon dioxide.

(2) *Kjeldahl's Method* (Dyer's modification). 0·5–1 grm. of the substance is placed in a hard glass flask (200–300 c.c.) with a long neck, into which penetrates the stem of a funnel used to cover the flask (Fig. 17). 20 c.c. of concentrated sulphuric acid (66° Bé.) and

[1] In this case the copper spiral can be rapidly reduced by heating it over a large non-luminous gas flame and dropping it into a thick-walled test-tube containing ½ c.c. of ethyl or, better, methyl alcohol; the tube is immediately closed by a rubber stopper through which passes a glass tube. The latter is connected with a pump until the spiral is cold.

a drop of mercury (which acts as a catalytic oxidising agent) are added, and the contents of the flask are heated, at first gently and finally more strongly, until vigorous boiling sets in. 10 grms. of potassium sulphate are then added, a little at a time, the heating being continued until the liquid is decolorised, by which time the whole of the nitrogen is transformed into ammonium sulphate. After the flask has been allowed to cool, its contents are washed out with water into a flask already containing 200–300 c.c. of water. 3–4 grms. of zinc dust (which decomposes ammoniacal compounds of mercury and prevents bumping by the evolution of hydrogen) are then added, and the flask closed with a rubber stopper through which passes a tapped funnel containing 120–160 c.c. of concentrated sodium hydroxide solution (30–35 per cent.) and a glass bulb (Figs. 18 and 19) communicating with a simple condensing tube dipping into a flask containing a measured volume of standard sulphuric acid and a drop of methyl orange. In order to prevent spurting of the caustic soda and its introduction into the condenser tube, the glass bulb is fitted with a delivery tube curved towards the wall of the bulb; it is, however, as well to push into this tube, almost as far as the bulb, a small plug of glass-wool or asbestos. Solutions of soda more concentrated than 35 per cent. often lead to spurting. About one-half the liquid is distilled and the excess of sulphuric acid remaining in the collecting flask determined by titration with alkali. Hence the amount of ammonia fixed by the acid can be calculated and so the percentage of nitrogen in the substance analysed. In Figs. 17 and 19 are shown forms of apparatus with which it is possible to carry out several determinations simultaneously.

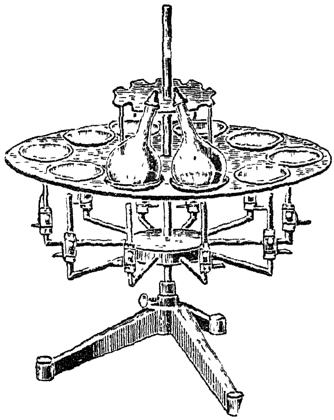


FIG. 17

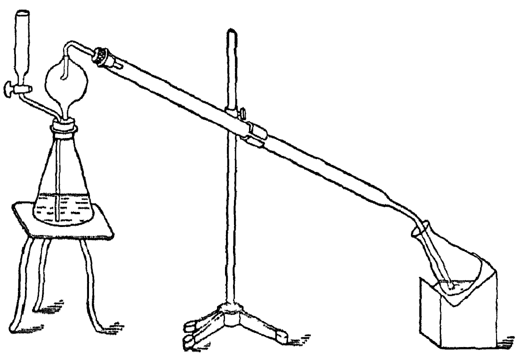


FIG. 18.

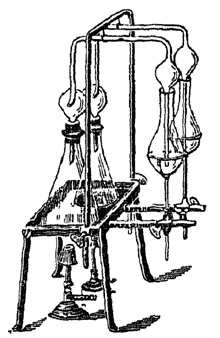


FIG. 19.

Kjeldahl's method cannot be used for the analysis of organic substances which contain nitrogen either united to oxygen (nitro compounds) or forming part of a pyridine or similar nucleus (quinoline, &c.)

(3) *Will and Varrentrapp's Method.* This method is based on the principle that almost all nitrogenous organic substances (which do not contain nitrogen linked to oxygen, such as the nitro-compounds), when they are heated with an alkali hydroxide or, better, with *soda lime* (*see* vol. i, p. 490), yield hydrogen, which transforms the nitrogen into ammonia. Little use is made of this method to-day.

QUANTITATIVE DETERMINATION OF THE HALOGENS. The method most commonly used is that of Carius. The substance (0·15–0·2 grm.) is weighed out in a small tube, which is then introduced into a large, hard glass tube 30–40 cm. long and 2–3 cm. wide, closed at one end and containing about 2 c.c. of fuming nitric acid and about 0·5 grm. of solid silver nitrate; this introduction is effected in such a way that the acid does not enter the small tube. The large tube is then softened near the open end by heating in the blow-pipe flame and gradually drawn out to a point, the walls of the tube being

allowed to thicken during the fusion (Fig. 20, *B*, shows the upper part of the tube on a larger scale). After being allowed to cool in a vertical position, the tube is introduced into a thick-walled iron sheath, which is closed with a screw-cap. It is then safe to incline the tube and introduce it into a bomb-furnace (Fig. 21), which holds four or more tubes and is raised slightly at one end; this is heated for 4–6 hours, the temperature being raised gradually to about 250°. Sometimes the tubes burst owing to the great internal pressure, but without danger from flying fragments of glass owing to the protection of the iron sheaths and of the folding shutters at the ends of the furnace, these being lowered during the heating.

At the end of the operation, when the tube is cool, it is taken from the iron sheath, held in a vertical position and its point (Fig. 20, *A a*) softened in a Bunsen flame. When the pressure in the tube has been thus relieved, a scratch is made with a file at the point marked *b*, and the file-mark touched with a red-hot glass, with the result that the upper part of the tube breaks off. The tube is then carefully emptied and washed out into a beaker with water, the small tube, held in pincers or a piece of platinum wire, being well washed inside and outside before removal. The liquid is heated and the precipitated silver

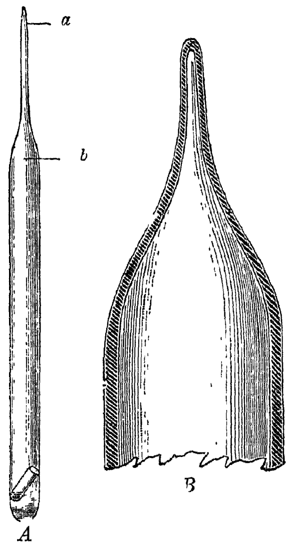


FIG. 20

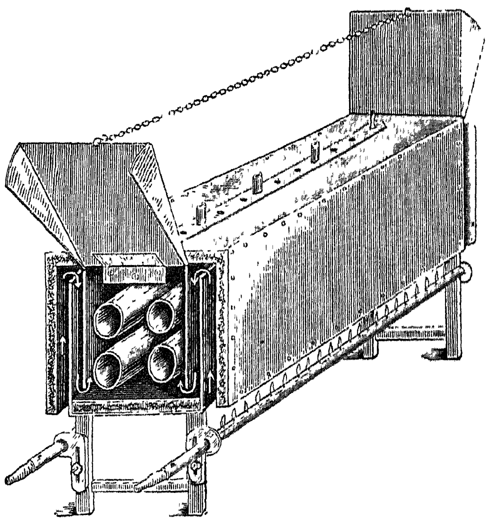


FIG. 21.

halogen compound is then collected on a filter, washed, dried in an oven, detached from the filter and heated in a weighed porcelain crucible until it just begins to melt. After being allowed to cool in a desiccator, the crucible is weighed and the amount of halogen contained in the organic substance calculated from the weight of silver haloid.

QUANTITATIVE DETERMINATION OF SULPHUR AND PHOSPHORUS. This is carried out by the Carius method in the same way as for halogens, except that no silver nitrate is introduced into the tube. At the end of the heating, the sulphur is obtained as sulphuric acid or the phosphorus as phosphoric acid, estimation of the amounts of these acids being effected by the ordinary methods. The halogens, sulphur and phosphorus, may also be determined after fusion of the substance with pure sodium peroxide.

CALCULATION OF THE EMPIRICAL FORMULA. From the results of the elementary analysis of an organic substance can be calculated the *percentage composition*, *i.e.* the quantity of each component in 100 parts of substance. To deduce the chemical formula, that is, the proportions in which the different atoms enter into the molecule, the percentage weight of each component is divided by the corresponding atomic weight, the numbers

thus obtained giving the proportions between the numbers of atoms of the different elements.

These numbers sometimes give directly the numbers of atoms contained in the molecule, but in other cases they represent multiples or submultiples of the real numbers of atoms.

If, for example, *lactic acid* is analysed, the percentage composition is found to be: C, 40 per cent.; H, 6·6 per cent.; O, 53·4 per cent; by dividing these numbers by the corresponding atomic weights, the following numbers are obtained: C, 3·3 (*i.e.* $\frac{40}{12}$); H, 6·6 ($\frac{6 \cdot 6}{1}$); and O, 3·3 ($\frac{53 \cdot 4}{16}$). These proportions have a common factor, 3·3, and division by this gives 1C, 2H, and 1O, *i.e.* CH_2O, which is an empirical *minimum* or *formula*, the simplest formula expressing the proportions between the numbers of atoms of the different elements.

This minimum formula does not, however, represent the molecular magnitude, and, in fact, analyses of formaldehyde, acetic acid, grape sugar, &c., give the same percentage composition and the same minimum formula, CH_2O, which must hence be a submultiple of the formulæ of these substances.

A knowledge of the percentage composition is not sufficient to determine the true molecular formula; the molecular magnitude, *i.e.* the molecular weight, must also be known in order to permit of a choice between the various multiples. By making use of one of the methods described in vol. i, "Inorganic Chemistry" (pp. 39, 81 *et seq*), the molecular weight of lactic acid is found to be 90, so that, of the various possible formulæ, CH_2O (mol. wt. 30), $C_2H_4O_2$ (mol. wt. 60), $C_3H_6O_3$ (mol. wt. 90), $C_4H_8O_4$ (mol. wt. 120) .... $C_6H_{12}O_6$ (mol. wt. 180), &c., only $C_3H_6O_3$ corresponds with lactic acid. But even this formula and the empirical formula tell nothing concerning the grouping of the atoms in the molecule which, as is explained in the following pages, is given by the constitutional formula.

DETERMINATION OF THE MOLECULAR WEIGHT BY CHEMICAL MEANS

In lactic acid one-sixth of the hydrogen can be substituted by a metal, so that there must be at least six (or a multiple of six) atoms of hydrogen in the acid, the empirical formula being necessarily at least trebled, giving $C_3H_6O_3$. To ascertain if this is the true formula, a derivative of the acid is prepared, such as the silver salt, which can easily be obtained pure. Analysis of this salt shows it to contain 54·8 per cent. of silver, and the atomic weight of silver being 107·7, calculation indicates that the residue of the lactic acid combined with 107·7 parts of silver weighs 89. Assuming that only 1 atom of silver has entered the lactic acid in place of 1 of hydrogen (as can, indeed, be deduced from the fact that the quantity of hydrogen in the salt is five-sixths of that originally present in the acid), the weight of the lactic acid would be 89 + 1, or 90. The true formula of the acid would hence be that corresponding with a molecular weight of 90, *i.e.* $C_3H_6O_3$.

For acid substances in general this *chemical method* may be employed for determining the molecular weight, making use of the silver salt and determining if the acid is mono-, di-, or tri-basic (that is, ascertaining if the silver replaces 1, 2, or 3 atoms of hydrogen), the calculation being then based on the presence of 1, 2, or 3 atoms of silver in the salt.

For basic substances, the molecular magnitude may be determined chemically by analysing the *platinichlorides*, the formulæ for which are always of the type of that of ammonium platinichloride: $PtCl_4(NH_3{\cdot}HCl)_2$, the ammonia being replaced by the organic base, which is mono- or di-acid, according as it replaces one or two molecules of ammonia in the platinichloride.

For other (indifferent) organic substances derivatives are prepared by substituting chlorine atoms for one or more hydrogen atoms, the proportion of chlorine being then estimated; the calculation is then similar to that described above.

The *chemical method* for determining the molecular magnitude does not always give certain results: experimental difficulties sometimes occur and often entail great labour.

Consequently the determination of molecular weights is usually effected by *physical methods*: vapour density method, cryoscopic method, ebullioscopic method, &c., these being all described and illustrated in vol. i (Part I).

POLYMERISM

It sometimes happens that the analysis of different substances shows them to have the same percentage composition, although their chemical and physical properties are different; thus, for example, acetic acid, lactic acid, glucose, &c., contain the same elements, C, H, and O, in the same proportions, there being $2n$ hydrogen atoms and n oxygen atoms for every n carbon atom. Accurate study of these compounds and determination of the molecular magnitude (molecular weight) shows that the differences depend on the true formulæ being multiples of the minimum or empirical formula. Thus, whilst the molecule of acetic acid is represented by $C_2H_4O_2$, that of lactic acid corresponds with $C_3H_6O_3$, and that of glucose with $C_6H_{12}O_6$. These molecules are hence all multiples of a hypothetical complex CH_2O, the ratios (but not the absolute quantities) between carbon, hydrogen, and oxygen being the same (1 : 2 : 1) in all cases. These compounds are termed *polymerides* and the phenomenon is known as *polymerism*.

In some instances, however, it happens that the molecular magnitude is not sufficient to differentiate certain compounds, which, besides containing the same elements in the same proportions (equal percentage compositions), have also the same molecular magnitudes, although differing in their physical and chemical properties. To explain the existence of these isomeric compounds, the chemical nature of carbon must be studied more in detail.

VALENCY OF CARBON, ISOMERISM, AND CONSTITUTIONAL FORMULÆ

On the foundation of multivalent radicles,[1] discovered by Odling, and of the investigations of Frankland (1852), which showed that nitrogen, phosphorus, and other elements easily formed compounds with three or five equivalents of other elements, Kekulé, in 1857 and 1858, accurately developed the true conception of *valency*, showing the constant tetravalency of carbon and thus widening the horizon of organic chemistry and originating the remarkable theoretical and practical development of the past half-century.

[1] Theory of Radicles and Types. In the first twenty years of last century, various compounds were discovered which stood in apparent contradiction to the electro-chemical theory of *dualistic formulæ*, put forward by Berzelius (vol. i. p. 44); in fact, in certain compounds, the hydrogen (electro-positive) was replaced by chlorine (electro-negative) without appreciably changing the chemical characters of the original compounds. It was then that chemical combinations came to be represented by *unitary formulæ*, no account being taken of the grouping of the atoms in the molecule.

But gradually, as the number of new organic substances increased, certain analogies became evident in their chemical behaviour. In studying cyanogen Gay-Lussac (1815) had indeed met, in various reactions and in various substances, the residue or radicle CN, which behaved as a monovalent element (like the halogens), combining with one atom of different monovalent metals, &c. In 1832 Liebig and Wöhler discovered and studied a monovalent atomic group or radicle, *benzoyl*, C_7H_5O, which was found in oil of bitter almonds combined with an atom of hydrogen (C_7H_6O); on oxidation by the air, this essence became transformed into benzoic acid, $C_7H_6O_2$, which with PCl_5 gave benzoyl chloride, C_7H_5OCl, and this, in its turn, gave the aldehyde C_7H_6O, when treated with nascent hydrogen, or benzoic acid under the action of water. All these compounds contain the monovalent benzoyl nucleus, C_7H_5O, which passes unchanged from one to the other by combining with monovalent atoms or groups. In 1833, in a classic work, Bunsen studied another radicle, *cacodyl*, which is a monovalent organic arsenic residue, $As{<}^{CH_3}_{CH_3}$. Later, in 1837, Dumas advanced and developed the *theory of radicles*, studying and classifying organic compounds with reference to the different radicles contained in them, these radicles thus coming to be considered almost as the *elementary substances of organic chemistry*. The condensation of simple radicles then leads to a compound radicle, forming a complex which can unite with other atoms or atomic groups. Liebig supported this new theory, whilst Berzelius strenuously opposed it, reproaching Dumas for regarding all chemical combinations as due to reciprocal interchanges of radicles.

Dumas and, still more so, Laurent, as a consequence of the discovery of new substances, arrived logically at the *theory of substitution*, which admits the possibility of replacing, one by one, the elements forming the radicle or

Kekulé and, independently of him, Cooper brought to light another most important property of carbon, resulting from its four equivalent valencies; they showed that carbon atoms possess also the property of combining directly one with another, in a greater or less number, mutually saturating one, two, or even three valencies and forming varying chemical compounds. For convenience, we represent these compounds graphically, placing the carbon atoms in an open or closed chain and saturating the valencies remaining free with other elements (usually hydrogen and oxygen). We have thus a series of groups differing according as the atoms united in a chain are few or many (even more than 30), according to whether the chain is branched by means of lateral chains, and also according as the valencies saturated between carbon and carbon are 1, 2, or 3.

If we represent the valencies of carbon by strokes, the valencies of the different carbon

nucleus of certain compounds by other elements or by radicles of other compounds (Dumas termed this phenomenon of substitution *metalepsy*).

Not only the hydrogen and oxygen but also the carbon of the radicles could, according to Laurent, be replaced by other radicles or other elements, *e.g.* by chlorine, without the fundamental characters of the original substances being substantially changed.

These last consequences of the *theory of substitution in radicles* (Dumas) or in nuclei (Laurent) were combated not only by Berzelius, but even by Liebig, who attempted to cover these new conceptions with ridicule and published in his "Annalen" (1840) a pungent satire in the form of a letter from Paris which was signed "S. C. H. Windler" (*Schwindler* being the German for swindler!), and which made the astonishing statement that it had been found possible to replace all the atoms of the molecule of manganese acetate by the corresponding number of chlorine atoms, the resulting substance retaining the characters of the original salt, although formed of chlorine alone; further, on the basis of the new theory, it was concluded that the chlorine used in England to bleach textiles replaced the hydrogen, oxygen, and carbon, and that already chlorine was being spun for the manufacture of nightcaps, which were greatly appreciated!!

Nevertheless, the new conceptions triumphed with the aid of numerous discoveries, which served to confirm, more and more, the ideas of Laurent and Dumas. And with the studies of Gerhardt, new horizons were opened to organic chemistry, which for so many years found a solid basis in Laurent and Gerhardt's (1852) *theory of types*, these clearing up the nebulous ideas then still held on the atom and the molecule; and it is due to these two investigators that Avogadro's work, denied by everybody, finally assumed the important position accorded to it in modern chemistry.

All organic and inorganic compounds were explained by comparing them with simple types of inorganic substances of well-known constitutions. The fundamental types of Gerhardt were four in number. $\left.\begin{matrix}H\\H\end{matrix}\right\}$, $\left.\begin{matrix}H\\Cl\end{matrix}\right\}$, $\left.\begin{matrix}H\\H\end{matrix}\right\}O$, $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$.

It was supposed that all the principal chemical compounds then known were derived from these types by simple substitution of the hydrogen by other elements and radicles. From the first type can be derived, for example, hydrocyanic acid, $\left.\begin{matrix}CN\\H\end{matrix}\right\}$, ethane, $\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}$, ethyl cyanide, $\left.\begin{matrix}C_2H_5\\CN\end{matrix}\right\}$, &c.; from the second, sodium chloride, $\left.\begin{matrix}Na\\Cl\end{matrix}\right\}$, ethyl chloride, $\left.\begin{matrix}C_2H_5\\Cl\end{matrix}\right\}$, acetyl chloride, $\left.\begin{matrix}C_2H_3O\\Cl\end{matrix}\right\}$, and so on. With the third type correspond, for example, sodium hydroxide, $\left.\begin{matrix}Na\\H\end{matrix}\right\}O$, nitric acid, $\left.\begin{matrix}NO_2\\H\end{matrix}\right\}O$, acetic acid, $\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O$, nitric anhydride, $\left.\begin{matrix}NO_2\\NO_2\end{matrix}\right\}O$, acetic anhydride, $\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O$, &c.

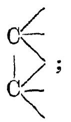
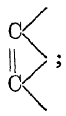
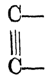
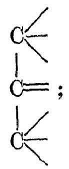
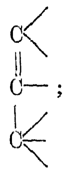
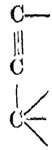
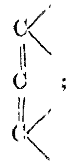
From the fourth type, Hofmann and Wurtz deduced theoretically and prepared in the laboratory a large number of compounds, part or all of the hydrogen atoms of ammonia being replaced; for example, ethylamine $\left.\begin{matrix}C_2H_5\\H\\H\end{matrix}\right\}N$, diethylamine, $\left.\begin{matrix}C_2H_5\\C_2H_5\\H\end{matrix}\right\}N$, trimethylamine, $\left.\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right\}N$, acetamide, $\left.\begin{matrix}C_2H_3O\\H\\H\end{matrix}\right\}N$, &c.

To explain the existence of polybasic acids and various other substances, Odling, Williamson, and Kekulé had recourse to *multiple types*, sulphuric acid being regarded as derived from the double water type $\left.\begin{matrix}H\\H\end{matrix}\right\}O \atop \left.\begin{matrix}H\\H\end{matrix}\right\}O$ $\left.\begin{matrix}H\\SO_2\\H\end{matrix}\right\}\begin{matrix}O\\O\end{matrix}$, and similarly succinic acid $\left.\begin{matrix}H\\C_4H_4O_2\\H\end{matrix}\right\}\begin{matrix}O\\O\end{matrix}$, &c.; for glycerol, a triple type was assumed, and so on.

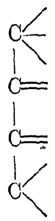
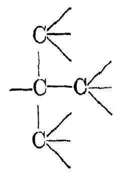
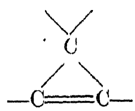
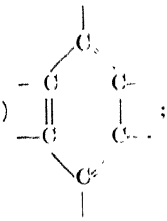
In 1856 Kekulé introduced another very important type, that of marsh gas, $\left.\begin{matrix}H\\H\\H\\H\end{matrix}\right\}C$, with tetravalent carbon, to which he referred numerous organic compounds; also certain compounds can be referred both to marsh gas and to ammonia, for example, methylamine, $\left.\begin{matrix}CH_3\\H\\H\end{matrix}\right\}N$, or $\left.\begin{matrix}NH_2\\H\\H\\H\end{matrix}\right\}C$, and from these different methods of considering the constitution and the reference to different types, were deduced various processes for preparing one and the same compound from different starting materials.

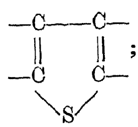
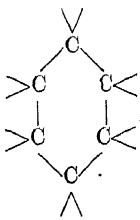
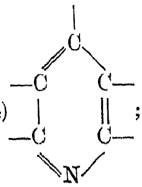
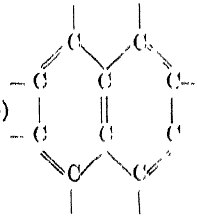
atom chains are given by the number of free valencies which are not used in uniting the carbon atoms among themselves and which can be saturated by different elements (usually H, O, N), giving rise to an enormous number of organic compounds.

The following are some of these hypothetical carbon atom chains :

(1)  ; (2)  ; (3)  ; (4)  ; (5)  ; (6)  ; (7)  ;

Hexavalent Tetravalent Divalent

(8)  ; (9)  , &c. (10)  ; (11)  ;

(12)  ; (13)  ; (14)  ; (15) 

Among these chains are two (Nos. 8 and 9) containing four carbon atoms and having equal numbers of free valencies. By saturating these ten free valencies with ten H atoms two compounds are obtained (these have actually been prepared) which contain equal numbers of C and H atoms, and have therefore the same percentage composition and the same molecular weight.

The physical and chemical differences of these two compounds, termed isomerides, are explained by the different grouping or linking of the atoms in the molecule. *In their chemical transformations, isomerides give up or exchange quite different atomic groups or atoms,* owing to the different functions and positions occupied by these atoms or groups in the molecule.

It is hence not sufficient to represent organic compounds by an empirical molecular formula, the **structural or constitutional formula,** deducible from the graphic representation of the chains illustrated above, being necessary in many cases to distinguish between isomerides.

To decide which of two isomeric formulæ should be assigned to a given substance, various chemical reactions are carried out with the substance, study of the new products indicating the constitutional formula.

An example will render these ideas clear : It is found that *ethyl alcohol* (ordinary liquid alcohol) and gaseous *methyl ether* have different physical and chemical properties, although they possess the same percentage composition and the same molecular magnitude, represented by the formula C_2H_6O. The constitutions or internal molecular structures of the two compounds are determined by a study of the following chemical reactions : treatment of the alcohol with hydrochloric acid gives first a compound C_2H_5Cl (ethyl chloride), one atom of monovalent chlorine having replaced one atom of oxygen and one of hydrogen or a hydroxyl residue, OH. By means of nascent hydrogen, the chlorine atom of ethyl chloride can be replaced by a hydrogen atom, giving the compound C_2H_6 (ethane). These reactions are hence expressed by the following equations :

(1) $C_2H_5 \cdot OH + HCl = H_2O + C_2H_5Cl$; (2) $C_2H_5Cl + H_2 = HCl + C_2H_6$; but ethane can have only the constitution, $\begin{matrix} H \\ H- \\ H \end{matrix} \!\!>\! C-C \!<\!\! \begin{matrix} H \\ -H \\ H \end{matrix}$, *i.e.* CH_3-CH_3, so that the alcohol will have the constitution $\begin{matrix} H \\ H- \\ H \end{matrix} \!\!>\! C-C \!<\!\! \begin{matrix} OH \\ -H \\ H \end{matrix}$

On the other hand, it is found, by various reactions, that the six hydrogen atoms of methyl ether present no difference one from another, and, no matter under what conditions hydriodic acid acts on the ether, it eliminates the oxygen as water, and another product is obtained which contains only one carbon atom in the molecule: The reaction hence takes place according to the equation:

$$C_2H_6O + 2HI = 2CH_3I + H_2O.$$

It is evident, then, that in methyl ether the six hydrogen atoms are united homogeneously to the two atoms of carbon and that the carbon atoms are joined, not directly, but indirectly, by means of an oxygen atom, which is readily eliminated. The constitutional formula of methyl ether will hence be:

$$\begin{matrix} H \\ H- \\ H \end{matrix} \!\!>\! C-O-C \!<\!\! \begin{matrix} H \\ -H \\ H \end{matrix} \quad \text{or} \quad CH_3-O-CH_3.$$

Use is not always made of constitutional formulæ, since they are not simple and are often inconvenient to write; hence attempts are made to simplify them by indicating the more important groups or residues contained in the molecule and giving at the same time an idea of the constitutions and of the functions of these groups; this is done by means of the so-called *rational formulæ*. The rational formula of ethyl alcohol will be $C_2H_5 \cdot OH$, in which the monovalent OH residue, characteristic of all the alcohols, is separated; that of acetic acid will be $CH_3 \cdot COOH$, the group COOH being characteristic of and common to all organic acids, &c.

METAMERISM. Constitutional and rational formulæ explain clearly isomerism in general and also the special case bearing the name *metamerism*. When, to an atom of a polyvalent element are united one or more groups in their different isomeric forms, we have special cases of isomerism for definite groups of substances.

For example, in the compound, $N \!<\!\! \begin{matrix} C_3H_7 \\ -H \\ H \end{matrix}$, the monovalent group $-C_3H_7$ may be present in its isomeric forms, *i.e.* either as $-CH_2-CH_2-CH_3$ or as $-C \!<\!\! \begin{matrix} CH_3 \\ -H \\ CH_3 \end{matrix}$. Although there is considerable resemblance between these two compounds, their different constitutions are manifested in certain chemical and physical properties. The following compounds are also *metameric isomerides*: $N \!<\!\! \begin{matrix} CH_3 \\ -C_2H_5 \\ H \end{matrix}$ and $N \!<\!\! \begin{matrix} CH_3 \\ -CH_3 \\ CH_3 \end{matrix}$; in fact, although the percentage compositions and molecular magnitudes are the same in both cases, the substituent groups of the ammonia molecule are different and the compounds belong to different categories—disubstituted and trisubstituted ammonias.

PSEUDOISOMERISM, TAUTOMERISM, DESMOTROPY. A substance sometimes contains atomic groups that occupy a very precarious (labile) position, since they exert certain influences one on the other and under certain given conditions can react in different ways, giving now one new substance and now another; this explains how it is that some compounds having a well-defined chemical character can, under some conditions, behave like substances with other chemical characters, without it being necessary to

assume a true change of constitution. Thus, for example, some of the derivatives of cyanic acid, $CN \cdot OH$, behave like derivatives, sometimes of the formula $N{\equiv}C{-}OH$ and sometimes of the formula $NH{=}C{=}O$, when the hydrogen atom is replaced by a given radicle. The same is the case for derivatives of cyanamide, $N{\equiv}C{-}NH_2$, and of carbodiimide, $NH{=}C{=}NH$; and of the two non-nitrogenous types, $-C(OH){=}\overset{|}{C}{-}CO{-}$ and $-CO{-}\overset{|}{C}H{-}CO$, where a hydrogen atom oscillates between the two carbon atoms. These compounds exist usually in only one form, the more stable one, but in the derivatives this stable form, simply on heating, is transformed into the labile one. For this phenomenon Baeyer proposed the name *pseudoisomerism*, and others that of *desmotropy*.

These forms can be distinguished sometimes by chemical reactions, but more generally by the molecular refraction, dielectric constant, magnetic rotation, electrical conductivity, &c.

In various substances, where several hydroxyls are present in more or less adjacent positions, there is often a tendency for intramolecular transformation to take place with condensation of two of these groups and separation of a molecule of water, giving rise to isomeric anhydrides, ethers, ketones, or alcohols, &c. In their turn, these derivatives or isomerides, which can be transformed one into the other, give rise to distinct classes of compounds, and this species of isomerism is called **tautomerism.**

STEREOISOMERISM OR ISOMERISM IN SPACE. We have already seen that, by the tetravalency of carbon and its property of uniting with itself to form various chains, it is possible, in certain cases, to explain the existence of isomerides, which have the same percentage composition and molecular magnitude, but different groupings within the molecules. Many cases of isomerism, foreseen from theoretical considerations, have since been actually met with and different isomerides have been prepared artificially after their existence had been foretold.

For a long time, however, certain compounds were known for which ordinary isomerism did not provide any explanation; among these the most important, from an historical point of view also, are the four dihydroxysuccinic acids (*tartaric acids*), of which two (ordinary tartaric acid and racemic acid) were studied by Berzelius as long ago as 1830. To these must be added lævo-rotatory tartaric acid and mesotartaric acid discovered by Pasteur. All these compounds have the same internal grouping of the atoms, although they are isomerides; it is not possible to distinguish between them by chemical reactions, but they can be clearly differentiated by their physical behaviour: they form *hemihedral*, *i.e.* symmetrical, but non-superposable crystals (related as an object to its image in a mirror): they have, too, different actions on polarised light, the plane of which is turned to the right by some and to the left by others. These acids are hence known as *physical* or *optical isomerides.*

Pasteur attempted to explain this isomerism by supposing the atomic groups to be arranged unsymmetrically in the molecule, in some cases in a dextro-rotatory spiral and in others in a lævo-rotatory spiral, or arranged at the *vertices of an irregular tetrahedron.*

When other similar isomerides—the lactic acids—had been discovered, J. Wislicenus, in 1873, suggested that isomerism of this kind could be explained only by *regarding the groups or atoms of these compounds as arranged in space so as to form distinct configurations.*

This isomerism in space (*stereoisomerism*) was explained by van 't Hoff and Le Bel (1874), independently, by means of the hypothesis of the *asymmetric carbon atom.* The starting-point of this hypothesis was Kekulé's idea (1867) of regarding, for the sake of convenience, the carbon atom as situated at the centre of a regular tetrahedron, and its four affinities as directed towards the four vertices, *i.e.* arranged homogeneously in space (Figs. 22, 23). If these affinities are satisfied at the vertices by monovalent atoms or atomic groups, the following cases present themselves: no isomerism is possible in the compounds Ca_3b, Ca_2b_2, Ca_2bc, and Cab_2c, where a, b, and c indicate either atoms other than carbon or groups of atoms (I, H, OH, &c.); the compound CH_2I_2 exists in only one form, and if we put the four atoms (H_2 and I_2) at the apices of the carbon tetrahedron, no matter

how their positions may be changed, it is not possible to find two different, *i.e.* non-superposable arrangements. If, however, the four groups or atoms combined with the carbon atom are all different, *e.g.* *Cabcd*, two isomerides are possible and in this case the carbon atom is termed *asymmetric;* in fact, if these atoms or groups are arranged, in one case, so that the circle *a*, *b*, *c* has a sense opposite to that in which the hands of a clock move (Fig. 24, I) (called, therefore, *dextro-rotatory isomerides*, and indicated by *d*- or by the sign +) and, in the other, in the opposite sense (Fig. 25 II) (termed *lævo-rotatory isomerides*, like levulose and indicated by *l*- or −), two non-congruent configurations are obtained; these cannot be superposed, one on the other, so that the same groups occupy the same

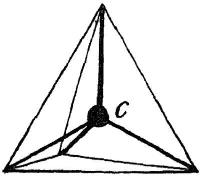


Fig. 22.

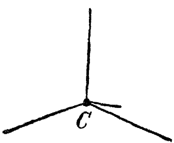


Fig. 23.

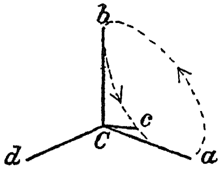


Fig. 24 I.

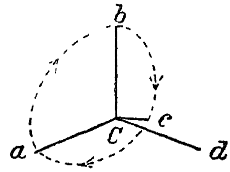


Fig. 25 II.

positions in the two cases. These two figures represent two different isomerides and are related in the same way as an object to its mirror-image or as the left hand to the right. This isomerism is called *enantiomorphism.*

These two different arrangements of the atoms round the asymmetric carbon atom also explain how it is that when polarised light traverses these molecules, its plane of polarisation is rotated, in one case to the right and in the other to the left. Van 't Hoff and Le Bel pushed their deductions still further, and showed that the dextro-optical deviation should be numerically equal to the lævo-optical deviation of the corresponding isomeride. This has been confirmed practically, and it also follows that when a pair of such isomerides are mixed in equal proportions, there should result an optically neutral mixture, thus giving rise to a special inactive or *racemic* isomeride. *A substance with only one asymmetric carbon atom always gives three stereoisomerides* (for example, three lactic acids).

It has also been deduced theoretically and proved practically that *all optically active compounds contain at least one asymmetric carbon atom,*[1] although not all compounds containing asymmetric carbon atoms are optically active, since the molecules may contain groups which neutralise each other's activity.

Many examples illustrating these principles will be discussed later in the special part of this book; meanwhile mention may be made of the most important of these com-

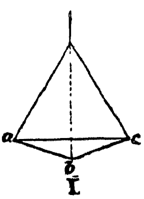


Fig. 26.

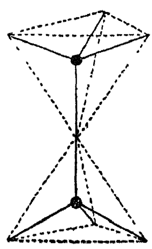


Fig. 27.

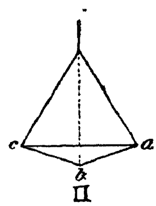


Fig. 28.

pounds: *leucine, asparagine, coniine,* the *lactic acids* (hydroxypropionic acids), &c., which contain one asymmetric carbon atom and give, in each case, three *stereoisomerides.*

These cases of stereoisomerism, and those which follow, will be understood more easily if studied by means of cardboard tetrahedra with differently coloured vertices.

When the substance contains two asymmetric carbon atoms, the number of stereoisomerides increases as follows:

If we take two tetrahedra like that shown in Fig. 26 I and Fig. 28 II, representing two similar molecules containing only one asymmetric carbon atom in which the groups

[1] Or else an asymmetric atom of nitrogen (*see later*) or sulphur, tin, &c. The exceptions to this rule are very rare and uncertain, one of the cases most discussed during recent times (1909–1910) being 1-*methylcyclohexylidene-4-acetic acid*, which does not appear to contain an asymmetric carbon atom, but is optically active.

a, b, and c, satisfying three of the valencies, are arranged in a dextro-rotatory sense, and superpose one tetrahedron on the other, so that the free valencies satisfy one another, there results a new isomeride, *i.e.* a molecule with two dextro-rotatory asymmetric carbon atoms, as shown in Figs. 27 and 29.[1]

If we join two lævorotatory carbon atoms (Fig. 28 II), that is, the mirror images of Fig. 26 I, a lævo-rotatory isomeride (Fig. 30 II) is obtained.

Finally, if one dextro-rotatory (Fig. 26 I) and one lævo-rotatory asymmetric carbon atom (Fig. 28 II) are united, a third stereoisomeride is obtained, which is permanently optically inactive (Fig. 31 III), the effect produced on polarised light by one asymmetric carbon atom being destroyed by the effect of the other.

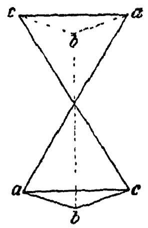

I

FIG. 29.

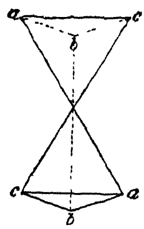

II

FIG. 30.

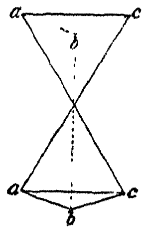
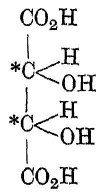
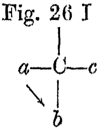
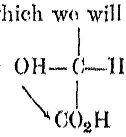
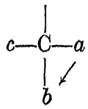
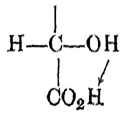

III

FIG. 31.

In order to understand these stereochemical speculations better, we will apply them to the isomerism of *tartaric acid*, which has the formula $C_4H_6O_6$, and contains two asymmetric carbon atoms (marked with asterisks) to which are joined the groups OH, CO_2H, and H:



If, for the letters a, b, and c of the tetrahedra considered above, we substitute the groups OH, CO_2H, and H, and if the tetrahedron of Fig. 26 I (which we will call $+A$) be represented as if projected on to a plane, thus:  or  (dextro-rotatory), and that of Fig. 28 II ($-A$), thus:  or  (lævo-rotatory), we arrive at the following stereoisomerides of tartaric acid:

I. By joining two $+A$ atoms, we get d-tartaric acid (Fig. 29 or 32 I).

II. By joining two $-A$ atoms, we get l-tartaric acid (Fig. 30 or 32 II).

III. By joining one $+A$ atom with one $-A$ atom, we have the permanently inactive mesotartaric acid (i-tartaric acid), as can be seen in Fig. 31 III, or 32 III.

IV. By mixing, mechanically, equal parts of acid I (+) and II (−), there results *racemic acid*, apparently inactive, but from which, by mechanical means (by hand with the aid of a lens), the two forms of crystals can be separated.

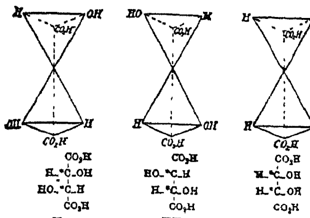
It is often assumed that the two asymmetric carbon atoms can rotate independently, on the common axis joining them, so that if the groups of one asymmetric carbon atom exert an attraction or influence on those of the other, a most *favourable position* could be attained, a chemical reaction being sometimes possible between one group and another

[1] Looking at the order in which the letters a, b, and c come in the two asymmetric carbon atoms, it would seem that these are not dextro-rotatory, but this is because the upper carbon atom has been turned through 180° from its position in Fig. 26; if its base is brought down, its identity with the other dextro-rotatory atom becomes evident.

with separation of, say, water and loss of the freedom of rotation ; to the new isomerism thus created we shall refer shortly.

STEREOISOMERISM IN DERIVATIVES WITH DOUBLY LINKED CARBON (ALLOISOMERISM). By means of the tetrahedra, we can show a double linking between two carbon atoms by arranging one side of one tetrahedron (carbon atom) in contact with a side of the other (Fig. 33).

With such an arrangement, even without asymmetric carbon atoms, isomerism is possible. In fact, a compound ${}^{a}_{b}\!>\!C=C\!<^{a}_{b}$ forms the following isomerides : (1) that



I II III

FIG. 32.

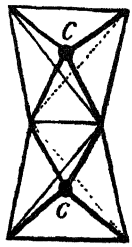


FIG. 33.

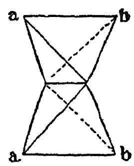


FIG. 34.

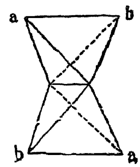
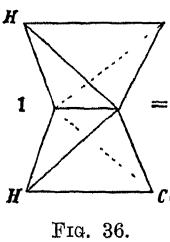


FIG. 35.

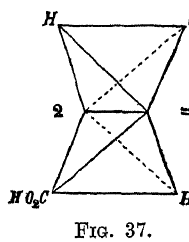
shown in Fig. 34, where the two similar atoms or groups of atoms, *e.g.* a and a, although united to two different carbon atoms, occupy adjacent positions: $\begin{array}{c} a\text{—C—}b \\ \| \\ a\text{—C—}b \end{array}$, or *cis*-positions (*cis-isomerism*) ; such a molecule exhibits *plane-symmetry*, the two pairs of similar groups lying to the left and right, respectively, of the perpendicular plane containing the common side (double linking) ; (2) that shown in Fig. 35, where two similar groups occupy non-adjacent or diagonally opposite or *trans*-positions $\begin{array}{c} a\text{—C—}b \\ \| \\ b\text{—C—}a \end{array}$, this form exhibiting *centro-symmetry.*

Similarly, a compound of the type, ${}^{a}_{c}\!>\!C=C\!<^{a}_{b}$, forms two isomerides, the *cis*-form, $\begin{array}{c} a\text{—C—}b \\ \| \\ a\text{—C—}c \end{array}$, and the *trans*-form, $\begin{array}{c} a\text{—C—}b \\ \| \\ c\text{—C—}a \end{array}$.



$= \begin{array}{l} HC\ CO_2H \\ \quad \| \\ HC.CO_2H \end{array}$

FIG. 36.



$= \begin{array}{l} HO_2C.CH \\ \quad\ \ \| \\ \quad HC.CO_2H \end{array}$

FIG. 37.

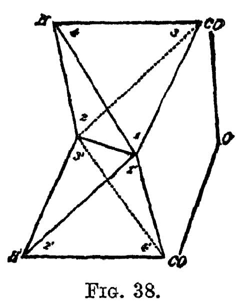


FIG. 38.

The best illustration of this type of isomerism is afforded by the two isomerides : *maleic acid* (*cis*-form, Fig. 36) and *fumaric acid* (*trans*-form, Fig. 37).

From these figures it is seen that the *cis*-form, maleic acid, should lend itself to the ready formation of *anhydrides* (condensation of two molecules or acid groups with separation of one molecule of water), since the two acid groups, CO_2H, are very near to one another, and it is, indeed, found that maleic acid easily gives an anhydride with separation of one molecule of water (Fig. 38), whilst no anhydride of fumaric acid is known.

Isomerism of this kind is exhibited by various substances, *e.g.* *crotonic* and *isocrotonic acids* ($CH_3 \cdot CH : CH \cdot COOH$) ; *mesaconic* and *citraconic acids* [$CH_3 \cdot C(COOH) : CH \cdot COOH$], &c.

Baeyer found that cases of isomerism similar to those just described occur also with *cyclic* compounds (*see* Part III), *i.e.* closed-chain compounds with simple linkings between

the carbon atoms. He distinguishes with the sign Γ compounds containing true asymmetric carbon (*absolute asymmetry*), adding the sign + or − if the compound is optically active; while he gives the name *relative asymmetry* to that shown by compounds with doubly linked carbon atoms (*alloisomerism*) or by cyclic compounds with simple linkings, the term *cis* or *trans* being added to the Γ. Thus, to the name tartaric acid would be added the sign $\Gamma+$ or $\Gamma-$ according as the acid is dextro- or lævo-rotatory, and to the name maleic acid Γ^{cis}, to fumaric acid Γ^{trans}, &c.

STEREOISOMERISM OF NITROGEN. Le Bel attempted to explain the isomerism of certain nitrogen compounds (*e.g.* methyl-ethyl-propyl-isobutyl-ammonium chloride) by assuming *absolute asymmetry* for the nitrogen atom. A more plausible explanation seems, however, to be afforded by the idea of *relative asymmetry* of the nitrogen, analogous to that of carbon atoms when united by double linking; in this way V. Meyer, Hantzsch, Werner, and others easily explained the isomerism of the oximes, hydroxamic acids, phenylhydrazones, &c. In general, a substance of the constitution $\begin{matrix} Cab \\ \parallel \\ Nc \end{matrix}$ should give two isomerides which can be represented as shown in Fig. 39; the *syn*-series (Fig. 39 I) and the *anti*-series (Fig. 39 II).

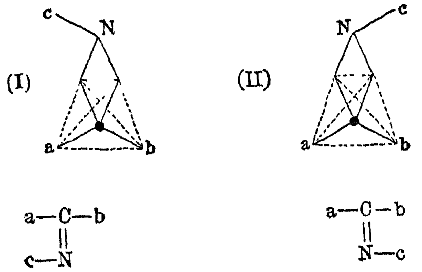


FIG. 39.

These investigators also studied those cases of isomerism in which the nitrogen behaves as a pentavalent element.

SEPARATION AND TRANSFORMATION OF STEREOISOMERIDES. Stereoisomerides and, in general, compounds containing asymmetric carbon atoms, when prepared artificially in the laboratory from inactive substances, are inactive, the *racemic configuration*, composed of a mixture of the *optical antipodes* in equal quantities, being formed. When, however, these substances are elaborated in the animal or vegetable organism, they are usually optically active.

The transformation of one of these optical antipodes into the other corresponding with it may sometimes be effected by passing through halogen derivatives, separation of the halogen from which results in the formation of the isomeride of opposite optical activity.

The separation of the antipodes, or of one of them, from the racemic isomeride was carried out by Pasteur (1848) in various ways. The following are the methods used at the present time:

(1) By fractional crystallisation (*see above*) of the racemic isomerides or of some of their salts at various temperatures and from various solvents, the antipodes can be separated directly or else they crystallise in hemihedral forms which can be readily separated. For some substances, it is convenient to prepare compounds with alkaloids (optically active basic compounds, *e.g.* strychnine, cinchonine, &c.), which, even when they do not form well-defined hemihedral crystals, can be easily separated by fractional crystallisation.

(2) By means of *enzyme* action (maltase, emulsin, &c.; *see* section on Fermentation), Fischer succeeded in resolving certain racemic glucosides. Much earlier than this, Pasteur discovered that certain bacteria or moulds (*Penicillium glaucum*, &c.) are capable of developing in a solution of the racemic substance at the expense of one of the optical antipodes, the other being left unchanged. This phenomenon is explained by the fact that bacteria owe their activity to certain substances which they produce (enzymes), and which are optically active and behave analogously to optically active solvents. Indeed, in many cases, stereoisomeric antipodes are separated by virtue of their different solubilities in an optically active solvent.

(3) With certain racemic compounds, the antipodes are separated by taking advantage of their different *velocities* of *esterification* in presence of an optically active alcohol; *e.g.* for racemic mandelic acid, menthol (which is an active alcohol) is used. For inactive alcohols, the velocity of esterification is the same for the two antipodes composing the racemic compound.

(4) When an optically active substance is heated within certain definite limits of temperature (*transformation point, see* vol. i, p. 190), it is often converted, to the extent

of one-half, into the oppositely active isomeride, so that an inactive mixture (racemic compound) is obtained; this takes place readily, for example, with the lactic acids. Above the transformation point the racemic substance may form inseparable *mixed crystals* (*see* vol. i, p. 111), the substance being then called *pseudo-racemic*. On the other hand, it has been shown that, with certain halogenated compounds, the transformation occurs even at ordinary temperatures, but with a minimum velocity; thus, with isobutyl bromopropionate, about three years is required.

(5) R. Stoermer (1909) found that the more stable form with the higher melting-point is often converted into the more labile form by means of the ultra-violet rays.

HOMOLOGY AND ISOLOGY

Turning to the more simple compounds, those formed from only carbon and hydrogen, we can easily see what procedure is necessary to arrive at those containing longer and more complex chains of carbon atoms. If we start from the most simple compound, *methane* (or marsh gas), CH_4, we can substitute an atom of hydrogen in it by other elements or even condense two of the monovalent CH_3 residues into one compound, $CH_3 \cdot CH_3$, thus obtaining *ethane* (C_2H_6). But in this compound we can also replace an atom of hydrogen by another —CH_3 residue, forming *propane*, $CH_3—CH_2—CH_3$ or C_3H_8, and by continuing this process we arrive at *butane*, $CH_3—CH_2—CH_2—CH_3$, *i.e.* C_4H_{10}; *pentane*, C_5H_{12}; *hexane*, C_6H_{14}, &c.

All the compounds of this series have analogous structures and have also many analogous chemical and physical properties; such a series is called a *homologous series*.

This series of the derivatives of methane can be represented by the general formula C_nH_{2n+2}, each term being the higher or lower homologue of the preceding or following term and differing from it by having one CH_2 complex more or less. If in all the simple compounds of this homologous series of methane we replace successively one hydrogen atom of the CH_3 group by the hydroxyl residue OH (characteristic of the alcohols) we obtain a homologous series of alcohols: CH_3OH, methyl alcohol; C_2H_5OH, ethyl alcohol, &c., and similar series can be obtained of aldehydes, acids, chloro-derivatives, &c.

The homologous compounds of each of these series differ always by CH_2 or by a multiple of it.

There are also other series with chains containing double linkings (*i.e.* compounds not completely saturated), and these unsaturated series are termed *isologous* with respect to the first, and, for an equal number of carbon atoms, they contain less hydrogen (C_nH_{2n} or even C_nH_{2n-2}).

Thus, ethane is isologous to the two-carbon-atom compounds of the unsaturated series, $CH_2{=}CH_2$ (ethylene) and $CH{\equiv}CH$ (acetylene), &c.

Homology is determined by the tetravalency of carbon, and in consequence the total number of hydrogen atoms in these compounds (hydrocarbons) is always even, *i.e.* divisible by two, and, if any of the hydrogen atoms are replaced by other elements, the sum of the atoms with odd valencies (Cl, P, N, As), and of the remaining hydrogen atoms should always give an even number.

PHYSICAL PROPERTIES OF ORGANIC SUBSTANCES IN RELATION TO COMPOSITION AND CHEMICAL CONSTITUTION

In many cases, certain physical properties are either common to whole groups of homologous or isomeric substances, or else vary gradually with change of chemical composition. So that the physical properties often contribute to the establishment of the true chemical constitutions of organic substances.

CRYSTALLINE FORM. The crystalline form of an organic compound is of considerable importance, since it often serves to distinguish clearly and accurately between two compounds. Two isomeric substances have often different crystalline forms.

There are, however, numerous cases of *dimorphism* or *polymorphism* (*see* vol. i), one of the forms always being more stable than the others.

We have already considered the relations existing between the crystalline form and chemical constitution in those stereoisomerides differing only by the *enantiomorphism* of their crystals.

P. Groth has discovered also the law of *morphotropy*, according to which a regular change is produced in the crystalline form of compounds by gradual substitution with new atoms or groups.

The relations between the crystalline forms and the chemical constitutions of substances have as yet, however, been little studied.

SOLUBILITY. The hydrocarbons and their substitution derivatives are but slightly or not at all soluble in water, but are almost all soluble in ether and in alcohol. Of the alcohols, the acids, and the aldehydes, the first terms of every homologous series are soluble in water, the solubility gradually decreasing as the number of carbon atoms in the molecule increases; these compounds are, however, relatively readily soluble in alcohol or ether. The polyhydric alcohols (glycerol, mannitol, &c.), are, however, soluble in water, but not in ether.

The compounds of the aromatic series are, in general, rather less soluble in alcohol and in water than the corresponding compounds of the fatty series.

In contact with two solvents which do not mix (*see* vol. i, p. 90), a substance dissolves in them both in a constant ratio, independent of the relative volumes of the two solvents, but depending on the concentration and on the temperature; thus, in separating by means of ether a compound dissolved in water, a better and more rapid result is obtained by shaking many times with a little ether each time than by using fewer, but larger, quantities of ether.

Of two isomerides, that with the lower melting-point is the more soluble.

SPECIFIC GRAVITY. Isomeric compounds have different specific gravities, but with the normal hydrocarbons (C_nH_{2n+2}), the values approach one another as the number of carbon atoms increases: at about $C_{16}H_{34}$ and for higher terms, the specific gravity becomes about 0·78. The specific gravity of the monobasic fatty acids is greater than 1 for the first terms of the series, but it diminishes with augmentation of the number of carbon atoms in the molecule.

MOLECULAR VOLUME. It was thought for many years that certain important rules could be deduced from the *molecular volumes* of organic compounds, that is, from the quotients, M/P, obtained by dividing the molecular weights (M) by the specific gravities (P).

In 1842 Kopp had found that, for liquids at the boiling-point, the molecular volume is very approximately equal to the sum of the atomic volumes of the component elements. For homologous compounds, the molecular volume increases by about 22 for every added CH_2 group. More recent studies (Lossen, R. Schiff, Horstmann, Traube, &c.) show, however, that these regularities are only relative and that isomeric compounds do not possess equal molecular volumes. In unsaturated series, every double linking increases the molecular volume and, with closed-chain compounds, the molecular volume is less than those of the corresponding open-chain compounds with double linkings. So that, in general, the molecular volume depends not only on *additive* factors (*e.g.* the sum of the atomic volumes), but also on *constitutive* factors (different linkings between the carbon atoms).

MELTING-POINT. Of two isomerides, that with the more symmetrical structure has the higher melting-point. The members of a series have varying melting-points, those with odd numbers of carbon atoms having lower melting-points than those immediately below them with even numbers. There are, in addition, other less important rules, but all present exceptions. A mixture of two substances, in suitable proportions, often has a melting-point lower than that of either of the components.

BOILING-POINT. In compounds of the same series, the boiling-point rises with increase of molecular weight, the amount of the increase being about 20° per CH_2 in the methyl alcohol or formic acid series and about 30° for benzene derivatives with methyl

groups in the nucleus. The boiling-points of isologous hydrocarbons, that is, those of the same number of carbon atoms but of different series (derivatives of methane, ethylene, and acetylene) are very close to one another.

Of the isomeric compounds of the aliphatic series, the normal one boils at the highest temperature and the boiling-point is increasingly lowered by increase in the branchings.

The substitution of hydrogen by halogens and by hydroxyl groups raises the boiling-point. The ethers boil at lower temperatures than the corresponding isomeric alcohols.

HEAT OF COMBUSTION AND HEAT OF FORMATION FROM THE ELEMENTS (*see* vol. i, pp. 60, 109, 372). The Hess-Berthelot law states that *the difference between the heats of combustion of two equivalent chemical systems is equal to the heat developed in the transformation of one system into the other*, that is, is equal to the *heat of formation from the elements* of this latter. In general, we can hence calculate the *heat of formation from its elements* of an organic compound by subtracting its heat of combustion from the sum of the heats of combustion of the elements composing it. As an example: the heat of combustion of methane, CH_4, at constant volume is 211,900 cals.; the heat of combustion of carbon ($C + O_2 = CO_2$) being 97,000 cals. and that of hydrogen ($H_2 + O = H_2O$) 68,400 cals., the complete combustion of methane is given by the following equation: $CH_4 + 2O_2 = CO_2 + 2H_2O = 97{,}000 + (2 \times 68{,}400) = 233{,}800$ cals., the sum of the heats of combustion of the component elements of methane. The heat of formation of methane will then be given by: $233{,}800 - 211{,}900 = 21{,}900$ cals., which also represents the heat necessary to resolve methane into its elements in order to initiate its combustion. The heat of combustion of ethyl alcohol being 340,000 cals., that of acetic acid 210,000, and that of ethyl acetate 554,000, the heat of formation of the last named from the first two will be · $340{,}000 + 210{,}000 - 554{,}000 = -4000$ cals.

In the analogous paraffin and olefine series, a difference of CH_2 corresponds with a variation of 150,000–160,000 cals. in the molecular heat of combustion.

The heats of combustion of isomeric compounds are equal, if they are chemically similar, for example, methyl acetate ($CH_3 \cdot CO_2CH_3$) and ethyl formate ($H \cdot CO_2C_2H_5$), but different if the compounds are of different molecular character (for example, allyl alcohol, $CH_2 : CH \cdot CH_2 \cdot OH$, and acetone, $CH_3 \cdot CO\ CH_3$), compounds with multiple linking in the fatty series having higher heats of combustion than the corresponding cyclic isomerides.

These calculations are also of importance for the evaluation of the energy produced in organisms by the transformations of various foods (*see also later* in the section on Explosives[1]).

HEAT OF NEUTRALISATION. With the *organic acids* this is the same for all, namely, 13,700 cals. (*see* vol. i, p. 97), as long as the resulting salts are not decomposed by water; with the *phenols* (cyclic compounds containing OH) the heat of neutralisation is about one-half the above value, or more if the acid character is intensified by the presence of the NO_2 group; with the alcohols it is almost zero.

[1] The following are the *heats of formation from the elements* of certain organic compounds, expressed in large calories per gramme-molecule:

Naphthalene, $C_{10}H_8$ · solid	−42	Cals.	Methyl alcohol, CH_3OH : liquid	62	Cals.
Nitronaphthalene, $C_{10}H_7NO_2$: solid	−14·7	,,	Ethyl alcohol, C_2H_5OH : liquid	70·5	,,
Dinitronaphthalene, $C_{10}H_6(NO_2)_2$: solid	−5·7	,,	Phenol, C_6H_5OH : liquid	34·5	,,
Trinitronaphthalene, $C_{10}H_5(NO_2)_3$ solid.	3·3	,,	Trinitrophenol (picric acid), $C_6H_2OH(NO_2)_3$ solid.	49·1	,,
Acetylene, C_2H_2 : gas	−61·4	,,	Sodium picrate, $C_6H_2ONa(NO_2)_3$: solid	117·5	,,
Ethylene C_2H_4 . gas	−15·4	,,	Ammonium picrate, solid	80·1	,,
Benzene, C_6H_6 : gas	−10·2	,,	Ether, $(C_2H_5)_2O$ gas	65·3	,,
Nitrobenzene, $C_6H_5NO_2$: liquid	4·2	,,	Ether, $(C_2H_5)_2O$ liquid.	72	,,
Dinitrobenzene, $C_6H_4(NO_2)_2$: solid	12·7	,,	Glycerol, $C_3H_5(OH)_3$: liquid	165·5	,,
Mannitol, $C_6H_{14}O_6$ · solid	320	,,	Trinitroglycerol, $C_3H_5(ONO_2)_3$: liquid	196	,,
Nitromannitol, $C_6H_8N_6O_{18}$: solid	179·1	,,	Cellulose (cotton), $C_6H_{10}O_5$: solid	227	,,
Mercury fulminate, $C_2N_2O_2Hg$: solid	−62·9	,,	Nitrocellulose, solid	624–696–706	,,
Anthracene, $C_{14}H_{10}$ · solid	−42·4	,,			

and the *heats of combustion* of various organic compounds are as follow. ethyl alcohol, 340 cals.; methyl alcohol, 182·2; mannitol, 727; cellulose, 680; terephthalic acid, 771; diphenyl, 1494, cane sugar, 1355; acetic acid, 210; benzoic acid, 772; ethyl acetate, 554; urea, 152; benzene, 779·8; dihydrobenzene, 848; tetrahydrobenzene, 892; toluene, 933; hexane, 991·2; methane, 211·9; ethane, 370·4; propane, 529·2; trimethylmethane, 687·2; ethylene, 333·4; propylene, 492·7; trimethylene, 499·4; isobutylene, 650·6; methyl chloride, 164·7; ethyl chloride, 321·9; propyl chloride, 480·2; chloroform, 70·5; dinitrobenzene (*o*-, *m*-, and *p*-), about 700; trinitrobenzene, 666—681; succinic acid, 357; azelaic acid, 1141; erucic acid, 3297; tribrassidinic acid, 10,236; glucose, 674; oxalic acid, 60·2; formic acid, 62·8; hydrocyanic acid, 152·3; naphthalene, 1233·6; phenol, 732; pyrogallol, 639.

OPTICAL PROPERTIES. (1) **Colour.** The majority of organic compounds are colourless, but if they contain iodine or the nitro-group or doubly linked nitrogen atoms (—N=N—), or two oxygen atoms directly united, they are generally coloured, especially in the aromatic series.

In the section on Dyes are given detailed illustrations of the remarkable relations between the chemical constitution of organic compounds and their colour.

(2) **Refraction.** This is the deviation produced in the direction of a ray of light (homogeneous; for example, sodium light) on passing through a transparent liquid, and varies with the substance. The *index of refraction n* varies with the temperature, and hence with the specific gravity (d) of the substance. The relation between these two values which gives the *refraction constant R* (or *specific refractivity*) is: $\frac{n^2-1}{n^2+2}\cdot\frac{1}{d} = R$, which is almost independent of the temperature. By multiplying by the molecular weight P, the *molecular refraction* is obtained: $M = \frac{n^2-1}{n^2+2}\cdot\frac{P}{d}$, this being constant for true isomerides and changing by a constant amount for a constant change in the composition.

The molecular refraction of a compound is approximately equal to the sum of the elementary atomic refractions, but here double and triple linkings have an influence, so that these can be detected in an organic compound by means of the refraction (true double linkings of the aliphatic series are often distinguished in this way from the cyclic linkings of benzene).

(3) **Polarised Light.** Owing to the importance of this phenomenon for whole groups of organic substances, it will be useful to recall briefly in a note[1] the fundamental ideas on polarised light.

[1] The luminous waves of white light are propagated in the cosmic ether with a velocity of about 300,000 kilometres per second, and there are physical instruments which admit of the measurement of the time required for a ray of light to traverse a few metres; indeed, Foucault measured the time taken by light to pass over a distance of 120 metres.

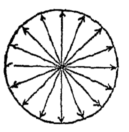


FIG. 40.

By studying the phenomena of interference of light rays, it can be shown that the vibrations of the ether in them are not longitudinal, *i.e* along the direction of propagation of the ray, but that the ether particles vibrate in all directions in a plane perpendicular to the direction of the ray (a transverse section of a ray is shown in Fig. 40), whilst the propagation of sound is effected by means of longitudinal vibrations in the direction of the path traversed by the sound.

A ray that enters a liquid or a non-crystalline solid, or a crystal of the regular system (cube or octahedron) gives only one refracted ray; when it enters a crystal of the rhombohedral system, *two* refracted rays are formed, one *extraordinary* and the other *ordinary*; when a ray enters a crystal of any other system, *two* refracted rays are formed, but these rays both behave like the *extraordinary* ray, and, like the latter, they do not obey the laws of refraction, according to which an incident ray, perpendicular to a medium with parallel faces, should not be deviated or refracted.

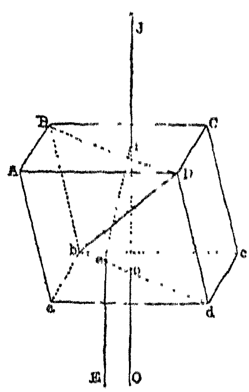


FIG. 41.

If a ray of light, Ji (Fig. 41) strikes a rhombohedral crystal of Iceland spar perpendicularly to the face $ABCD$, the ray divides into two. The one, ioO, continues in the same direction, the other, ie, is deviated, but when it emerges from the crystal assumes the direction eE, parallel to the original direction. The two parallel rays leaving the crystal have equal luminosities, but oO follows the ordinary laws of refraction (*vide supra*) and is called the *ordinary ray*, whilst the other, eE, does not obey these laws and is termed the *extraordinary ray*.

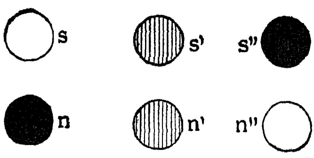


FIG. 42.

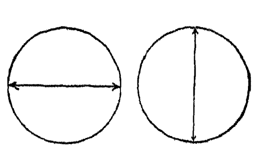


FIG. 43.

If the crystal is rotated about the incident ray Ji as an imaginary axis, the position of the ray oO does not change, whilst the ray eE moves in the sense in which the crystal is rotated. The extraordinary ray iE always lies in the plane of the *principal axis* of the crystal $dbBD$, which passes through the principal axis of the crystal bO and is parallel to it. These two rays emerging from the crystal have, however, properties different from those of the incident ray Ji; in fact, if either of the two refracted rays (eE or oO) is passed into a second rhombohedron of Iceland spar, two new rays (*double refraction*) are obtained, but the intensities of the two rays vary according to the relative positions of the two crystals. Thus, if a ray emerging from the first crystal passes perpendicularly into the second crystal, the principal section of which is parallel to that of the first, no double refraction is observed, only one ray leaving the second crystal (s in Fig. 42, the second hypothetical ray n not being visible and marked black in the figure). If, however, the second crystal is rotated round the imaginary axis, oO, a second ray (extraordinary) suddenly appears, *i.e.* double refraction takes place, and whilst the luminosity of the new ray increases,

Those organic substances are called *optically active* which rotate the plane of polarised light. Some substances are optically active in the crystalline state (not in the amorphous state or in solution), and hence the action on polarised light is due in these cases to the peculiar arrangement of the molecules; very few are active in both the crystalline and amorphous states, the majority exhibiting activity only in a dissolved condition (sugars, &c.), where the phenomenon depends on the arrangement of the atoms or groups of atoms in the molecule. This holds also for camphor and oil of turpentine, which are active even in the form of vapour.

The longer the layer (l) and the greater the concentration of the solution (p = grammes of dissolved substance in 100 of solution) traversed by the polarised light, the greater will be the rotation of the plane of polarisation. Referring the observed rotation a to a length of 10 cm. of a solution containing 1 grm. of pure substance in 1 c.c. ($= pd/100$, where d is the specific gravity of the solution), we get the *specific rotatory power* of the solution for the yellow sodium light (D line of the spectrum [1]) by means of the following formula: $[a]_D = \frac{100\,a}{l \cdot d \cdot p}$. For active liquid substances examined without solvent, $[a]_D = \frac{a}{l \cdot d}$. The *molecular rotation* (for a molecular weight M) is given by: $[M] = \frac{M \cdot [a]}{100}$.

For a definite solvent and given concentration and temperature, every active substance (and such are almost all those containing *asymmetric carbon, see* p. 26) has a constant and characteristic specific rotatory power, either to the right (+) or to the left (−). This varies with the nature and degree of electrolytic dissociation of the solvent, and increases with dilution and diminishes with rise of temperature; for purposes of comparison, it is usually determined at 20°, and is then indicated thus: $[a]^{20}_{D}$. By repeating the determinations and using moderately high concentrations, the influence due to the solvent is determined and, on subtracting this, the *true specific rotation* is obtained. Freshly prepared solutions of certain sugars exhibit the phenomenon of *muta-rotation*, which, however, disappears after a time or on boiling the liquid, the normal rotation then being given.

This important property of optically active compounds is studied by means of special apparatus termed *polarimeters*, which are used particularly in the analysis of sugars (and hence often called *saccharimeters*), and will be described in the section dealing with this group of substances.

MAGNETIC ROTATORY POWER. All liquids in a magnetic field produce a greater or less rotation of the plane of polarised light, according to their chemical composition and in conformity with the laws governing the refractivity of light. In many cases the constitution of a substance has been determined or confirmed by determining the *molecular magnetic rotation.*

ELECTRICAL CONDUCTIVITY. We must refer the reader to the detailed treatment of electrolytic dissociation and the theory of ions in vol. i (pp. 91 *et seq.*), as the same is directly applicable to organic compounds, especially as regards the conductivity of salts, acids, bases, &c.

that of the first ray becomes weaker and when the principal sections of the two crystals form an angle of 45°, the two rays have equal intensities (s', n'); if the crystal is rotated still more, the extraordinary ray becomes more luminous, whilst the first (*ordinary*) decreases in luminosity, and when the principal sections are perpendicular to one another, the intensity of the ordinary ray (s'') is zero (*i.e.* it is not seen), only the extraordinary ray being seen with its maximum intensity (n''). The light rays emerging from the second rhombohedron are hence different from those emerging from the first, these latter not varying in intensity when the prism is rotated, whilst the others do so.

The rays leaving the first prism are called *polarised*, and are distinguished from ordinary light rays, since, on passing through a second prism, they undergo the changes described above. A polarised ray passes as an *ordinary ray* through a second rhombohedron only when its *plane of polarisation* is parallel to the principal section of the new rhombohedron. It is found, then, that the plane of polarisation of the polarised ordinary ray is perpendicular to the plane of polarisation of the extraordinary ray. Hence, the rays E and O vibrate in planes perpendicular to one another (Fig. 43).

POLARISATION BY REFLECTION. Polarised light rays are obtainable, not only by double refraction, but also *by reflection* under special conditions, namely, when a light ray falls on a plate of glass at an incident angle of 54° 35′.

Polarised light is also obtained by simple refraction, by passing a ray of light through a series of superposed parallel plates or sheets of tourmaline.

[1] The angle of rotation varies with the length of the light-wave and is greater for violet rays (which have a smaller wave-length and are hence refracted more) and less for red rays (which have a greater wave-length and are hence less refrangible).

CLASSIFICATION OF ORGANIC SUBSTANCES

These are usually divided into two large series :

(1) That of the *open-chain* carbon compounds or *methane derivatives*, termed also compounds of the *fatty* or *aliphatic series*, as all the fats and many of their derivatives belong here. This series embraces two groups of substances ; that of the *saturated compounds* or *derivatives of the paraffins* (C_nH_{2n+2}) and that of the *unsaturated compounds* (*olefines*, C_nH_{2n} and derivatives of *acetylene*, CH_{2n-2}).

(2) That of the *closed-chain* carbon derivatives, this being subdivided into :

(*a*) The *isocyclic* or *carbocyclic compounds*, which have the closed chain formed either of nuclei of six carbon atoms with six available valencies to every nucleus (C_nH_{2n-6}, *benzene derivatives* or *aromatic compounds*) or from nuclei with different numbers of carbon atoms, but more highly hydrogenated (*cycloparaffins*, *cyclo-olefines*, and *polymethylene derivatives*).

(*b*) The *heterocyclic compounds*, the closed chain of which contains atoms (N, P, S, O, &c.) other than carbon.

The hydrogenated compounds of carbon are called *hydrocarbons* and are termed *saturated* when the carbon atoms are joined by single valencies, and the other valencies are all satisfied by hydrogen. These saturated hydrocarbons cannot combine with a further quantity of hydrogen.

Hydrocarbons containing carbon atoms united by double or triple linkings are called *unsaturated hydrocarbons*, and these can combine with further quantities of hydrogen, thus becoming saturated. Other important hydrocarbons are those with closed chains, which we shall study in Part III of this book.

Usually in homologous series, with increase in the number of carbon atoms, the compounds pass from the gaseous to the liquid and solid states ; *e.g.* formic acid, with one carbon atom, is a liquid and boils at 99°, while the homologous acid with six carbon atoms is a solid and boils at over 300°.

OFFICIAL NOMENCLATURE

With the continuous development of organic chemistry and the multiplication of new compounds, the need was often felt for a rational method of naming compounds which would facilitate the treatment of these vast numbers of compounds. And for the new nomenclature to be the more efficacious it needed to be international, because everywhere there reigned the greatest confusion in the naming of chemical compounds, this referring either to the starting substance or to the new group to which they belonged, or to the use for which they were intended, or to the molecular constitution, and so on, so that the same substances often had four or five names.

In 1892, at an International Convention of Chemists at Geneva, a general system of nomenclature of organic compounds was agreed on. This is gradually being introduced into chemical literature, and, although not always felicitous, it has helped to simplify the naming of compounds and to reduce the confusion.

Following only in part the ideas proposed by Kolbe many years before, the new nomenclature derives the names of all compounds from the names of the fundamental hydrocarbons to which the compounds can be referred, taking into account the number of carbon atoms present as well as the nature of the linking. Thus, to the fundamental names of the saturated hydrocarbons: methane, ethane, propane, butane, pentane, hexane, heptane, &c., the addition of the suffix *ol* indicates the presence of the hydroxyl group —OH, and thus an alcohol, for example, *methanol* (methyl alcohol), *ethanol* (ethyl alcohol), &c. ; the suffix *al* serves to denote the *aldehyde* group $\left(-\mathrm{C}\begin{smallmatrix}\diagup\!\!\diagup\mathrm{O}\\ \diagdown\mathrm{H}\end{smallmatrix}\right)$, thus, *e.g.* *methanal* = formaldehyde, *ethanal* = acetaldehyde, &c. ; the suffix *one* indicates the

ketonic group (—CO—), thus, *propanone* (commonly called acetone), &c. The suffix *oic* is used to indicate the organic *acids*, which all contain the characteristic *carboxyl* group $\left(-\ CO_2H,\ i.e.\ -C\begin{matrix}\nearrow O \\ \searrow HO\end{matrix}\right)$, and thus we have *methanoic* (formic) acid, *ethanoic* acid, *propanoic* (propionic) acid, *butanoic* acid, *pentanoic* acid, &c.

For the unsaturated doubly linked hydrocarbons the fundamental hydrocarbon ethylene is distinguished with the name of *ethene*, and that with a triple bond between the two carbon atoms (acetylene) is called *ethine*.

With the saturated hydrocarbons, isomerides with branched chains are referred to the *normal hydrocarbon* (*i.e.* non-branched) with the longest chain present in the molecule, numbering progressively its carbon atoms, starting at the end nearest to the point where branching occurs. The name begins with that of the residue of the side-chain,[1] then follow the successive numbers of the atoms of the normal chain where side-chains join on, and finally comes the name of the normal hydrocarbon.

$$\begin{array}{ccccc} (1) & & (2) & & (3) \\ CH_3 & — & CH & — & CH_3 \\ & & | & & \\ & & CH_3 & & \end{array}$$

bears the official name *methyl*-2-*propane* (some call it *propyl*-2-*methane*), and isopentane,

$$\begin{array}{ccccccc} (1) & & (2) & & (3) & & (4) \\ CH_3 & — & CH & — & CH_2 & — & CH_3 \\ & & | & & & & \\ & & CH_3 & & & & \end{array}$$

that of *methyl*-2-*butane*, &c.

When there are also secondary ramifications a supplementary numbering is used; thus, with isodecane,

$$\begin{array}{ccccccccccccc} (1) & & (2) & & (3) & & (4) & & (5) & & (6) & & (7) \\ CH_3 & — & CH_2 & — & CH_2 & — & CH & — & CH_2 & — & CH_2 & — & CH_3 \\ & & & & & & | & & & & & & \\ & & & & & (4^{I}) & CH & — & CH_3 & & & & \\ & & & & & & | & & & & & & \\ & & & & & (4^{II}) & CH_3 & & & & & & \end{array}$$

the official name would be metho-4^{I}-ethyl-4-heptane.

[1] The names of the *hydrocarbon residues*, called also *alkyl* groups, are formed from the root of the name of the corresponding hydrocarbon, with the suffix *yl*; thus, with methane corresponds the *methyl* residue CH_3; with ethane, *ethyl*, $—C_2H_5$; and then follow *propyl*, $—C_3H_7$; *butyl*, $—C_4H_9$, &c.

PART II. DERIVATIVES OF METHANE

AA. HYDROCARBONS

THE hydrocarbons form a very large and important group of organic substances, which are composed only of hydrogen and carbon, and give rise to other most varied substances by replacement of part or all of the hydrogen by other elements or groups.

For the reasons given on p. 28, they are divided into two main groups: saturated and unsaturated hydrocarbons.

(a) SATURATED HYDROCARBONS

These are called saturated because the linkings between the carbon atoms are simple ones and all the valencies are saturated, so that hydrogen, chlorine, bromine, iodine, ozone, &c., cannot be *added* to them; the halogens do, indeed, react with saturated hydrocarbons (fluorine reacts with methane even at −187°), but by *substitution* of the hydrogen atoms.

They are called also *paraffins*, since, like the common solid paraffins, all the saturated hydrocarbons resist, in the *cold*, the action of chromic acid, potassium permanganate, and concentrated nitric and sulphuric acids, and are, in general, compounds with an almost indifferent chemical character. In the hot, however, energetic oxidising agents convert them, more or less completely, into carbon dioxide and water.

As a general rule, these hydrocarbons are insoluble in water and only some of them dissolve in alcohol, whilst almost all are soluble in ether.

Of the *direct* or *continuous* (*normal*) and *branched* (isomeric) *open chains*, mention has already been made on pp. 15, 16, and 28, and it can be seen how, starting from the hydrocarbon, C_4H_{10}, the number of isomerides rapidly increases: 2 for butane; 3 for pentane, C_5H_{12}; 5 for hexane, C_6H_{14} (all known); while for $C_{12}H_{26}$ the number theoretically possible is 355 and for $C_{13}H_{28}$, 892, only some of which are, however, known. All the terms of the *paraffin series* can be represented by the general formula C_nH_{2n+2}, and the following Table (p. 31) gives the name, formula, boiling-point, and melting-point of the principal known paraffins. The official nomenclature is described on p. 28.

The first members of the series are gases, then follow liquids as far as C_{15}, and beyond that, solids, the boiling- and melting-points rising with increase of the molecular weight (*see* p. 24).

NATURAL FORMATION AND GENERAL METHODS OF PRODUCTION. These hydrocarbons, from the lowest gaseous members to the highest solid ones (paraffin), occur abundantly as the almost exclusive components of petroleum (especially that from America), and it is not difficult to separate single individuals from these complex mixtures.

In many natural emanations of inflammable gas, methane and, to some extent, ethane are found in large proportions, and the solid hydrocarbons occur also in *ozokerite* (*which see*).

The gaseous, liquid, and solid hydrocarbons are formed abundantly on the dry distillation of wood, lignite, bituminous schists, and coal, especially *boghead* and *cannel coals* which are relatively rich in hydrogen (*see* Illuminating

SATURATED HYDROCARBONS, C_nH_{2n+2}

(After hexane, only the *normal* ones are given)

		Melting-point	Boiling-point	Specific Gravity
CH_4	Methane	−184°	−164° (760 mm.)	0·415 (−164°) 0·555 (0°, 760 mm.)
C_2H_6	Ethane	−172·1°	−84·1° (749 mm.) (0° at 23·8 atm.)	0·446 (0°)
C_3H_8	Propane	−45°	−44·5° (0° at 5 atms.)	0·535 (0°, liquid)
C_4H_{10}	Butanes { normal	—	+ 1°	0·600 (0°)
	isobutane	—	−17°	0·6029 (0°)
C_5H_{12}	Pentanes { normal	−200°	+36·3°	0·454 (0°)
	isopentane	—	+30·4°	0·622
	tertiary	−20°	+ 9°	—
C_6H_{14}	Hexanes { normal	—	69°	0·6603 at 20°
	dimethylisopropylmethane	—	58°	0·666
	dimethylpropylmethane	—	62°	0·6766 (0°)
	methyldiethylmethane	—	64°	0·677
	trimethylethylmethane	—	49·6°	0·6488
C_7H_{16}	Heptane	—	98·3°	0·683 at 20°
C_8H_{18}	Octane	—	125·8°	0·702
C_9H_{20}	Nonane	−51°	150°	0·718
$C_{10}H_{22}$	Decane	−31°	173°	0·7467
$C_{11}H_{24}$	Undecane	−26°	196°	0·7581
$C_{12}H_{26}$	Dodecane	−12°	215°	0·7684
$C_{13}H_{28}$	Tridecane	− 6°	234°	0·775
$C_{14}H_{30}$	Tetradecane	+ 4°	252°	0·775
$C_{15}H_{32}$	Pentadecane	+10°	270°	0·776
$C_{16}H_{34}$	Hexadecane	18°	287°	0·775
$C_{17}H_{36}$	Heptadecane	22°	303°	0·777
$C_{18}H_{38}$	Octodecane	28°	317°	0·777
$C_{19}H_{40}$	Nonodecane	32°	330°	0·777
$C_{20}H_{42}$	Eicosane	37°	205°	0·778
$C_{21}H_{44}$	Heneicosane	40°	215°	0·778
$C_{22}H_{46}$	Docosane	44°	224°	0·778 at the melting-point
$C_{23}H_{48}$	Tricosane	48°	234°	0·779
$C_{24}H_{50}$	Tetracosane	51°	243°	0·779
$C_{25}H_{52}$	Pentacosane	53·5°	—	—
$C_{26}H_{54}$	Hexacosane	58°	— at 15 mm. pressure	—
$C_{27}H_{56}$	Heptacosane	60°	270°	0·780
$C_{28}H_{58}$	Octocosane	60°	—	—
$C_{31}H_{64}$	Hentriacontane	68°	302°	0·781
$C_{32}H_{66}$	Dotricontane (Dicetyl)	70°	310°	0·781
$C_{35}H_{72}$	Pentatricontane	75°	331°	0·782
$C_{60}H_{122}$	Hexacontane	101°	—	—

Gas); also when petroleum residues are strongly heated under pressure (*cracking*), hydrocarbons similar to petroleum and also gaseous ones are formed.

Of the numerous synthetical methods of preparation of the saturated hydrocarbons, the following more important ones may be mentioned:

(*a*) Any member of the series can be obtained by reducing the halogen derivatives of the hydrocarbon (obtained from the alcohols and the halogen hydracids) by means of *nascent hydrogen* (generated by sodium amalgam, or by a solution of sodium in absolute alcohol, or by zinc and hydrochloric acid, or by heating zinc and water at 160°) or by hydriodic acid, especially in the presence of red phosphorus (which transforms the iodine into hydriodic acid): $C_2H_5I + H_2 = HI + C_2H_6$; $C_2H_5I + HI = I_2 + C_2H_6$ (*see* Table of the halogen derivatives of the hydrocarbons).

(*b*) The alcohols give paraffins on being heated with hydriodic acid:

$$C_2H_5 \cdot OH + 2HI = H_2O + I_2 + C_2H_6.$$

(*c*) By the interaction of zinc alkyls and water:

$$Zn(C_2H_5)_2 + 2H_2O = Zn(OH)_2 + 2C_2H_6.$$

(*d*) From unsaturated hydrocarbons by the action of hydrogen, *e.g.* by heating acetylene and hydrogen at 400°–500°, or in presence of platinum-black.

(*e*) By eliminating a molecule of carbon dioxide from the organic acids and salts by heating with soda-lime or sodium alkoxide:

$$CH_3 \cdot COONa \text{ (sodium acetate)} + NaOH = Na_2CO_3 + CH_4.$$

(*f*) By the action of sodium or of zinc on the zinc alkyls or alkyl iodides in ethereal solution in a closed tube (Wurtz), two alkyl groups, even different ones, being condensed:

(1) $2CH_3I + Na_2 = 2NaI + C_2H_6$.

(2) $C_2H_5I + C_4H_9I + Na_2 = 2NaI + C_2H_5 \cdot C_4H_9$.

(3) $2CH_3I + Zn(CH_3)_2 = ZnI_2 + 2C_2H_6$.

(*g*) During the last few years it has been shown that magnesium is much more active than zinc in many organic syntheses (*see later*, Grignard Reaction), and with alkyl iodides dissolved in absolute ether, magnesium forms magnesium alkyl salts which, on decomposition by means of water or dilute acid or ammonia with solid ammonium chloride, yield the saturated hydrocarbons: $C_2H_5I + Mg = C_2H_5MgI$, and this $+ H_2O = C_2H_6 +$ $Mg(OH)I$. In part, however, the magnesium fixes the halogen, and then two alkyl residues condense, forming a hydrocarbon of double the number of carbon atoms:

$$2C_2H_5I + Mg = MgI_2 + C_4H_{10}.$$

(*h*) Sabatier and Senderens' catalytic process, for which *see* pp. 34 and 59.

(*i*) By electrolysing acetic acid:

$$\begin{matrix} CH_3\text{—}COOH \\ \\ CH_3\text{—}COOH \end{matrix} = \begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix} + 2CO_2 + H_2$$

the hydrogen going to the negative pole and the hydrocarbon and carbon dioxide to the positive one.

METHANE (MARSH GAS), CH_4

This is a gas which is often found ready formed in nature, and in former times it was always confused with hydrogen (inflammable air). Pliny refers to the gases which exude from the earth in certain regions and are inflammable (these are probably the *sacred fires* of the ancient Chaldeans). Basil Valentine (1500) records fires in mines preceded by the emanation of asphyxiating, poisonous vapours, which are dispersed and rendered innocuous by the fire issuing from the rock. Also Libavius (1600) speaks of the inflammable and explosive gas of mines, and in 1700–1750 history records numerous explosions, especially in coal-mines. In was Volta who, in 1776, when studying

the same gas, which is also evolved in marshes, showed that it differed from hydrogen, since in burning it requires double its volume of oxygen and forms carbon dioxide. In 1785 Berthollet proved that the gas is formed of carbon and hydrogen, and later Henry, Davy, and Berzelius determined its true composition.

It occurs abundantly as exhalations from the earth near the Caspian Sea (sacred fires of Baku) and in the peninsula of Apsheron is used for heating purposes.

At Pittsburg there are great wells of pure methane, and it is found also at Glasgow, in the Crimea, and also in Italy, at Pietra Mala (Bologna), in Ferrarese, in Piacento (Salsomaggiore), &c. It always occurs in coal-mines, being formed from the coal by slow decomposition and remaining occluded in the coal under great pressure, together with carbon dioxide and nitrogen.

It is invariably developed in marshy places, where there is organic matter putrefying under water. It is found in the gas of the intestines of man and, still more, of the ruminants (about 50 per cent. CH_4), being produced by the action of enzymes on the cellulose of vegetable matter. Illuminating gas contains up to 40 per cent. of it.

PROPERTIES. It is one of the *permanent gases* (vol. i, p. 28); it liquefies at $-164°$ and solidifies at $-186°$. It has no colour or taste, but a faint garlicky odour. It dissolves slowly but appreciably in fuming sulphuric acid, but only very slightly in water (0·05 per cent.). It is readily inflammable and burns with a faintly luminous flame; mixed with oxygen it forms a *detonating mixture* (inflammable at 667°, whilst the mixture with ethane inflames at 616° and that with propane at 547°), the maximum effect being obtained with 1 vol. of methane and 2 vols. of oxygen ($CH_4 + 2O_2 = CO_2 + 2H_2O$).[1] Mixed with air, it forms the *firedamp* of coal-mines, which is very dangerous owing to its explosibility,[2] although it is not poisonous since miners can withstand an atmosphere containing 9 per cent. of methane; if there is not more than this proportion, it produces a kind of pressure at the forehead, which ceases immediately on breathing pure air.

By an electric charge or in a red-hot tube, it decomposes into carbon and

[1] Explosive gas mixtures (Teclu, 1907):

	Maximum effect	Minimum effect	
		With excess	With deficit
	Vols.	Vols.	Vols.
100 volumes of air + hydrogen	40	170	8–10
,, ,, ,, + methane	10	—	3·6
,, ,, ,, + coal gas	17–20	31	4·7
,, ,, ,, + acetylene	8·3	130	2 4
,, ,, ,, + ether vapour	3·3	8	1·5
,, ,, ,, + alcohol vapour	6·5	—	3·4

[2] Since the methane is occluded under great pressure between the layers of coal, its development and hence also the danger is greater when the atmospheric pressure diminishes or when the temperature rises. To prevent explosions of firedamp, the miners use the Davy lamp (vol. i, p. 377). Considerable danger of explosion more often exists in mines owing to the *coal dust* suspended in the air of the galleries and behaving like a *pyrophoric substance* (vol. i, p. 174); as a precautionary measure, air is continually circulated through the galleries by powerful fans, and the air and the walls are moistened by means of pulverisers. Hardy has constructed an apparatus which allows of the quantity of methane being determined from the sound produced by the mixture of air and methane in traversing an organ pipe. Mines containing much dust are dangerous even if the atmosphere is moist and the Davy lamp is used, since the particles of coal passing through the gauze into the lamp may issue in a red-hot condition. When mines are being excavated, *safety explosives* (*which see*) are used to avoid fires and explosions. Sometimes the coal ignites in certain parts of the mine; in such cases, work is not suspended, but these parts are isolated by walls and if the fire becomes threatening, recourse is had (usually with success) to the sealing of the mine and subsequent inundation with water or filling of the galleries with carbon dioxide. When an explosion occurs in a mine, a large amount of carbon monoxide is formed which poisons the workers, who can, however, sometimes be rescued if they can be made to breathe, sufficiently promptly, under a bell containing compressed air (Mosso's Method; vol. i, p. 175).

hydrogen, and a few unsaturated hydrocarbons, with traces of benzene and naphthalene.

PREPARATION IN THE LABORATORY. Besides by the general methods given above, methane is formed by passing a mixture of carbon monoxide or dioxide with hydrogen over reduced nickel (catalyst) heated at 250° (Sabatier and Senderens): $CO + 3H_2 = H_2O + CH_4$. Attempts have recently been made to put this method on an industrial basis, by transforming the carbon monoxide and dioxide of water-gas into methane (Ger. Pat. 183,412). Pure methane is formed by passing a mixture of carbon disulphide vapour and hydrogen sulphide over red-hot copper (Berthelot): $CS_2 + 2H_2S + 8\,Cu = 4\,Cu_2S + CH_4$; also by treating aluminium carbide with water: $C_3Al_4 + 12H_2O = 4Al(OH)_3 + 3CH_4$.

In the laboratory it is usually prepared from an intimate mixture of one part of crystalline sodium acetate with four parts of soda lime (or better, with four parts of baryta or with a mixture of anhydrous sodium carbonate and dry powdered calcium hydroxide). This is heated in a retort or in a hard glass tube until gas begins to be evolved, the temperature being then kept constant. As impurities, it contains a little hydrogen and acetylene, so that, before collecting the methane, the gas is passed over pumice moistened with concentrated sulphuric acid.

Chemically pure, it can be obtained, by the general method, from zinc ethyl and water.

INDUSTRIAL USES. For several centuries, the inflammable gases issuing from the earth and from petroleum have been utilised at Baku for heating lime-kilns. In North America, as far back as 1821, these natural emanations were used as illuminating gas. The most important discoveries, made at Pittsburg in 1882, resulted in 98 per cent. of the American production being obtained from this source in 1900; after 1905, the wells of Louisiana also acquired importance. The utilisation of the gas at the present day is carried out rationally and on a vast industrial scale, the gas (issuing from suitably constructed wells) passing to large gasometers which distribute it directly to over 500 factories and 40,000 houses, where it is employed for power, heating, and lighting (with the Auer mantle), the price being about 3½ cents per cubic metre. In Canada, 400 wells are being used, giving, in 1907, gas of the value of £120,000. In England, wells have been sunk since 1900 which yield 400,000 cu. metres of gas per day. The spring at Wels, in Austria, which gave 57,000 cu. metres of gas per day in 1894, yielded only 500 cu. metres in 1901. The gas utilised in the United States of America represents the following values in pounds sterling: in 1882, 40,000; in 1890, 1,400,000; in 1894, 2,800,000; in 1899, 4,000,000; and in 1906, 9,600,000. These gases have the sp. gr. 0·624–0·645, and a calorific value of 9000–10,000 cals. per cu. metre. The composition varies between the following limits: CH_4, 80–95 per cent.; H, 0·5–1·5 per cent. (sometimes 15 per cent.); C_2H_4, 0·3–4 per cent.; CO, 0–0·6 per cent.; CO_2, 0·3–2·5 per cent.; O, 0·35–0·80 per cent.; N, 0·5–3·5, together with traces of H_2S. The amounts of natural gas used at Baku were 46·5 million cu. metres in 1905, 96·3 million in 1906, and 117 million in 1907, the composition being: CO_2, 3–3·8 per cent.; C_nH_m, 1·2–2·6 per cent.; O, 7–7·6 per cent.; CH_4, 54·8–60·2 per cent.; H, 13·58–0·8 per cent.; and N, 20·4–25 per cent.

The gas which is used at Salsomaggiore (Piacenza) for public lighting purposes and which issues from the earth together with petroleum and saline waters containing iodine, has a specific gravity of 0·692, and the following composition (Nasini and Anderlini, 1900): CH_4, 68 per cent.; C_2H_6, 21 per cent.; heavy hydrocarbons, 1 per cent.; N, 8 per cent. In Italy, 1,520,000 cu. metres of these gases, of the value £2280, were used altogether in 1902, 6,737,500 cu. metres in 1908, and 8,270,000 cu. metres, of the value £8760, in 1909.

Important sources of these gases have been recently discovered in Hungary, England (at Heathfield a well gave as much as 500,000 cu. metres per day), and in Denmark (since 1872).

ETHANE, C_2H_6

This gas is found dissolved in crude petroleum and is one of the principal constituents of the North American gas-wells of Delamater, near Pittsburg.

It is a gas which can be liquefied at 0° by means of a pressure of twenty-four atmospheres and then has a sp. gr. 0·446; at the ordinary pressure it becomes liquid and boils

at $-84°$ and is solid and melts at $-172°$. It is almost insoluble in water; 1 vol. of absolute alcohol dissolves $1\frac{1}{2}$ vol. of it. It burns with a faintly luminous flame, and is more readily soluble than methane. In the laboratory it is prepared by the general methods already given (p. 32).

PROPANE, C_3H_8 (METHYLETHYL, $CH \cdot C_2H_5$ or DIMETHYLMETHANE, $CH_2(CH_3)_2$)

This is a gas like ethane and becomes liquid at $-44°$, or at $0°$ under five atmospheres pressure, the liquid at $0°$ having a sp. gr. 0 535; it solidifies and melts at $-45°$. It is slightly soluble in water, and absolute alcohol dissolves 6 vols. of it. With water under pressure and at temperatures below $0°$ it forms a solid hydrate, which decomposes at $+8{\cdot}5°$. The illuminating power of propane is about $1\frac{1}{2}$ times that of ethane. It is best prepared, in the laboratory, by reducing isopropyl iodide by means of the copper-zinc couple, or by reducing acetone or glycerol with hydriodic acid:

$$\underset{\text{glycerol}}{C_3H_5(OH)_3} + 6H = 3H_2O + C_3H_8 \quad \text{or} \quad \underset{\text{acetone}}{CH_3 \cdot CO \cdot CH_3} + 4H = H_2O + C_3H_8.$$

BUTANES, C_4H_{10} (Two Isomerides)

(*a*) *Normal Butane*, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_3$ (*diethyl*), is a gas which liquefies at $+1°$, and at $0°$ has a sp. gr. 0·600. It is found in Pennsylvanian petroleum, and is prepared in the laboratory by the ordinary methods (p. 32).

(*b*) *Isobutane*, $CH_3 \cdot CH\!<\!{}^{CH_3}_{CH_3}$ (*trimethylmethane* or *methylpropane*), is a gas which becomes liquid at $-115°$; it is contained in petroleum and is prepared by the usual methods in the laboratory.

PENTANES, C_5H_{12}

These hydrocarbons are found especially in the petroleum products boiling a little above $0°$, and are placed on the market under the names of *rhigolene* and *cymogen* for anæsthetic purposes and for the manufacture of artificial ice. The three isomerides predicted by theory are known:

(*a*) *Normal pentane*, $CH_3 \cdot [CH_2]_3 \cdot CH_3$, is a colourless, mobile liquid boiling at $+37{\cdot}3°$, having a sp. gr. 0·454 at $0°$, and solidifying only at about $-200°$; it is hence used for making low-temperature thermometers, and as a lubricant in the Claude liquid air machine (vol. i, p. 298). It occurs abundantly in Pennsylvanian petroleum.

(*b*) *Isopentane*, $\underset{\displaystyle CH_3}{CH_3 \cdot \underset{|}{CH} \cdot CH_2 \cdot CH_3}$ (methyl-2-butane or ethylisopropyl), is a light colourless liquid boiling at $30{\cdot}4°$, and having a sp. gr. 0·622 at $20°$. It is found in large quantities in petroleum, and can be prepared artificially from isoamyl iodide by the ordinary methods (p. 32).

(*c*) *Tetramethylmethane*, ${}^{CH_3}_{CH_3}\!>\!C\!<\!{}^{CH_3}_{CH_3}$ (dimethyl-2-propane), is found in the gases from petroleum, and is liquid at $+9°$ and solid at $-20°$. It can be obtained in the laboratory either by chlorinating acetone, $CH_3 \cdot CO \cdot CH_3$, by means of phosphorus pentachloride and treating the dichloropropane thus formed with zinc-methyl:

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}Cl\\Cl\end{matrix} + Zn\!<\!\begin{matrix}CH_3\\CH_3\end{matrix} = ZnCl_2 + \begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}CH_3\\CH_3\end{matrix},$$

or from tertiary butyl iodide by the action of zinc methyl:

$$2\,\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}CH_3\\I\end{matrix} + Zn\!<\!\begin{matrix}CH_3\\CH_3\end{matrix} = ZnI_2 + 2\,\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}CH_3\\CH_3\end{matrix}.$$

The constitutions of acetone and tertiary butyl iodide having been determined (*see later*), that of tetramethylmethane is fixed. And since the reduction of butyl iodide yields *isobutane*, the constitution of the latter is proved.

HEXANES, C_6H_{14}

The five isomeric hexanes which should exist are all known (*see* Table, p. 31). They are found particularly in *petroleum ether*, *gasolene*, and *ligroin* (*i.e.* in the portions of

petroleum boiling below 150°), together with *heptanes* and *octanes*. They are formed also from shaly coal like cannel coal and boghead.

HIGHER HYDROCARBONS

These are very numerous and are found in petroleum and in its residues (vaseline, paraffin, &c.); they distil unchanged (after C_{16}) only in a vacuum, the boiling-point being thus lowered by about 100°.

Many of these higher normal hydrocarbons were prepared synthetically by Krafft by reducing the corresponding fatty acids, alcohols, and ketones.

HEPTACOSANE, $C_{27}H_{56}$, and **HENTRIACONTANE,** $C_{31}H_{64}$, are found in beeswax and in American tobacco (about 1 per cent.), the former being also found in soot.

HEXACONTANE, $C_{60}H_{122}$, is the highest term of the paraffin series to be prepared synthetically by Hell and Hagele in 1889 by condensing 2 mols. of myricyl iodide, $C_{30}H_{61}I$, by fusion with sodium, which removes the iodine as NaI. It melts at 102°, is slightly soluble in alcohol or ether, and distils, to some extent unchanged, in a vacuum It has probably the normal structure and thus forms the longest carbon atom chain as yet prepared synthetically.

Some of the saturated hydrocarbons of the aliphatic series have important practical applications, especially as sources of light and heat. In illuminating gas are found the gaseous members, in petroleum the liquid, and in paraffin the solid ones.

A brief account of the industrial treatment of these three products will now be given.

ILLUMINATING GAS [1]

Illuminating gas and the other products of the dry distillation of coal vary in composition with the nature of the coal employed. In gas manufacture, account has to be taken of the value of the by-products: coke, tar, ammonia, &c., which sometimes contribute largely to the cost of manufacture. So that mixtures of coal are used which give good coke, the luminosity of the gas from certain coals being supplemented by mixing with others rich in hydrogen and fats, such as some of the very expensive English coals, like *cannel coal, boghead,* various shaly coals, &c. In general, coals used for making gas have compositions varying between the following limits: C, 78–85 per cent.; H, 5–8 per cent.; O, 6–13 per cent.; N, 1·2–1·9 per cent.; and S, 0·1–2 per cent., a high content of sulphur being harmful; they should leave little ash on burning, and preference is given to those containing considerable quantities of volatile products. The more hydrogen there is, the greater will be the useful yield, since every kilogram of hydrogen can gasify 4–5 kilos of carbon (according as more or less methane, ethylene, &c., is formed). Gas-coal giving good coke contains more than 15 per cent. of volatile products and less than 35 per cent.

[1] History. This industry began with the nineteenth century, its apotheosis being reached at the end of that century with the application of the incandescent gas-mantle From the year 900 the Chinese have employed petroleum vapour, distributed by wooden pipes, for lighting purposes. It was, however, only in 1739 that James Clayton, in investigating the causes of the emanation of inflammable gas often occurring in the Lancashire mines, heated coal in closed vessels and collected the gas (illuminating gas!) developed in large bladders. In 1767, Watson, in laboratory experiments on a small scale, obtained gas, ammonia, and coke by the distillation of coal. This was the time when coke was beginning to be employed in metallurgical operations, and in 1786 Lord Dundonald used the gas from the coke furnaces to light his house, and Pickel lighted his laboratory with the gas formed on distilling bones. More important trials were, however, made in England by W. Murdock, for the illumination of large works by distilling coal. Helped in his undertaking, first by Watt, the inventor of the steam-engine, and afterwards by his pupil Clegg, he succeeded in 1805 in extending lighting by gas to many establishments The distillation of wood was studied by the engineer F. Lebon, in France; and in 1799, a patent was taken out "for a new method of employing combustibles more efficiently, for heating or lighting, and of collecting the various products" Some days later, all Paris was admiring the gas-lamp which Lebon used to illuminate the gardens of the Hôtel Seignelay. Probably Lebon did not then foresee the wonderful development which was to take place in gas lighting in the nineteenth century or dream of the monument to be erected to him many years later in his native town, Chaumont, or of the statue which was dedicated to him in Paris in 1905.

It was when the use of large plant was attempted for lighting by gas that technical difficulties cropped up, inconveniences which were negligible on a small scale becoming insurmountable in the case of large works It was already noticed that the new illuminating gas burned with a rather sooty flame and disseminated unpleasant odours, whilst in the works the piping often became obstructed owing to solid distillation products being carried by the gas. If, in addition, we consider the popular prejudice to any innovation, aggravated by the fantastic propaganda of certain scientific men, especially in France, who exaggerated the danger of explosion, it is easy to conceive how unpromising the conditions of this industry were up to 1812. To Clegg is due the elimination of the main technical difficulties, the tarry matters carried along by the gas being removed by means of a number of

The *oxygen* present in coal gives rise to larger or smaller quantities of carbon dioxide and monoxide, and it cannot be denied that the monoxide is a powerful poison. Only 10–15 per cent. of the *nitrogen* present in the coal is transformed into ammonia, 20 per cent. being found in the gas and 60 per cent. in the coke, whilst 2–3 per cent. forms hydrocyanic acid and cyanides in the gas and tar. *Moisture* in the coal is harmful, since water causes an increase in the amount of carbon dioxide in the gas and also absorbs heat for its evaporation.

In order to judge of the value of the coal, distillations are carried out, in gasworks, in small laboratory retorts containing a weighed quantity of coal and heated at a very high temperature (900° and even higher); the gas and vapours are washed in bottles, first with lime-water and then with lead acetate, the pure gas being collected in a cylinder over mercury, so that it can be measured and its composition and illuminating power investigated. To judge of the practical value of a coal, use is made of the product of the yield of gas (that is, the number of cubic metres from 100 kilos of coal) and its candle-power. For any given coal, this product is almost constant; increase of the temperature of distillation resulting in a greater yield of gas, but of a lower illuminating power. Naturally this rule holds only between certain limits of temperature, which are never exceeded in practice.

Of various coals, the best is that which gives the highest value for this product, but account must also be taken of the yields of coke, ammonia, and tar, and of the specific gravity of the gas.

The temperature of carbonisation varies with the nature of the coal and, in general, with fatty coals (bituminous) the evolution of gas begins at 50°, and at a red heat vapours of liquid products pass over; at a higher temperature, gaseous products predominate.

The most convenient temperature usually lies between red heat (cherry-red) and yellowish white heat. In general, after an hour's heating (with a furnace at 1400°), the coal in the retort reaches 400°, after three hours 950°, and after five hours 1075°. On heating 1000 kilos of English coal at different temperatures the following results are obtained:

		At red heat	At bright orange red
(*a*) Gas obtained (cubic metres)		234	340
(*b*) Candle-power		20·5	15·6
(*c*) Candles per 1000 kilos = $a \times b$		4800	5300
(*d*) Composition:	Hydrogen	38·1 %	48 %
	Carbon monoxide	8·7 %	14 %
	Methane	42·7 %	30·7 %
	Heavy hydrocarbons	7·6 %	4·5 %
	Nitrogen	2·9 %	2·8 %

Gas prepared at a higher temperature has a lower calorific power.

cooled tubes, and further purification being effected by lime, the gas being then collected in large gasometers, from which it was distributed by pipes to the consumers. Thus, it became possible in 1813 to light part of London with coal gas, and in 1815 Winsor illuminated certain quarters of Paris.

Nobody on the Continent dared attempt a similar industry; everybody was distrustful, not foreseeing its great future and being frightened by the technical difficulties which met this, the first great chemical industry, for many years confined to England. It was in this country that it underwent the most rapid extension and perfection (in 1823, fifty-two towns were lighted by gas), the scientific and practical men giving it their entire support. In 1810 a powerful English company was founded by Clegg and became later the famous Imperial Continental Gas Association, which with a capital of £2,000,000 in 1824, £3,500,000 in 1874, £3,800,000 in 1897, and £5,000,000 in 1908, was formed with the view of undertaking the lighting of the principal European towns. Even to-day many towns are still pledged to contracts, as yet unexpired, with the great English companies. London itself, within the last few years, has found the greatest obstacle to the introduction of electric lighting in contracts with gas companies which have already made fabulous profits.

In Germany, the first small gas-plant was that of Lampadius in 1816, used for his own establishment, extension being subsequently effected as a result of the work of Flashoff and Dinnendhal. At Berlin the first attempt was made in 1829; then followed Hanover, and in 1884, 557 German towns were lighted by gas, the annual consumption of coal being 1,700,000 tons. In Austria the first plant was erected in 1818 by Prechtl. In America, Baltimore was illuminated by gas in 1806, Philadelphia in 1822, and New York in 1834. At Milan gas lighting was introduced in 1832.

After 1870 all the principal populous centres and even the small towns were lighted by gas, all objection to this form of illumination having disappeared; experience had shown that the expected terrible explosions of mixtures of gas and air did not occur and that the small accidents which did happen were not more serious than those occurring daily with paraffin lamps. The victory over petroleum, although furiously contested, was especially complete in the case of public lighting.

To this success have contributed, most of all, the incessant improvements of methods of manufacture, which have resulted in the supply of a purer, more abundant, and more economical gas.

The composition of gas varies also according as the heating is more or less prolonged.[1]

It will be seen that the diminution of luminosity is less proportionally than the increase in volume of the gas, and to-day the distillation is pushed to a temperature of 1100–1200°, this resulting in greater (absolute, not relative) quantities of light, luminous hydrocarbons and of hydrogen being obtained. It is hence important to employ suitable mixtures of coals, so that these may be impoverished as much as possible at a high temperature, the relatively low luminosity being compensated for by the addition of special fatty coals, as already mentioned, and also, at the present day, of benzene.

The duration of the distillation varies from 3 to 5 hours; the extra amount of gas that would be obtained by heating further would be insufficient to make up for the cost of heating. 100 kilos of Westphalian coal give about 71 kilos of coke, 4 kilos of tar, 5 kilos of ammonia liquors, and 17 kilos (30·5 cu. metres) of gas; loss, 3 kilos.

The **COMPONENTS OF ILLUMINATING GAS** obtained from coal are very varied and can be embraced in three groups: (*a*) *combustible diluents:* H, CH_4, CO; (*b*) *light-yielding gases and vapours:* ethane, ethylene, butylene, acetylene, crotonylene, allylene, pentylene, benzene, toluene, xylene, thiophene, styrene, indene, naphthalene, acenaphthene, fluorene, propane, butane, pyridine, phenols; (*c*) *inert or harmful impurities:* CO_2, NH_3, HCN, CS_2, COS, and N; naturally the majority of these substances are present only in traces.

The *quantitative composition by volume of the gas* usually varies between the following limits: CO_2, 1·25–3·20 per cent.; CO, 4·5–6·5 per cent. (for English coals, 6–9 per cent., and for German coals, occasionally 9–11 per cent.); H, 42–55 per cent.; CH_4, 32–38 per cent.; N, 1–3 per cent.; O, 0–0·5 per cent.; aromatic hydrocarbons (benzene, &c.), 0·8–1·4 per cent.; unsaturated hydrocarbons (ethylene, 2–2·5 per cent.; acetylene, 0·1–0·2 per cent.; propylene, 0·2–0·5 per cent., &c.) The specific gravity of gas varies from 0·350 to 0·500 (air = 1) and 1 cu. ft. of gas weighs rather more than half an ounce.[2] *The calorific power* of illuminating gas ranges, as a rule, from 4000 to 5000 cals. per cubic metre, thus producing the same heating effect as 3·43 kw.-hours. The illuminating power is discussed later.

PROPERTIES OF ILLUMINATING GAS. In addition to the lighting power, for which it is mostly used, to the heating power which makes it a valuable source of mechanical energy for gas motors, to the relatively low specific gravity which renders it useful in aeronautics, attention must be paid to the explosive properties of illuminating gas when mixed with air (*see* p. 33), and to its poisonous properties even when present in only 2 per cent. by volume. Its poisoning effect is due especially to the carbon monoxide present, but also, to some extent, to other components. When the first symptoms of poisoning are observed, fatal consequences can be prevented by vigorous respiration of pure air or, better, oxygen, while the use of compressed air according to Mosso's system also gives good results (vol. i, p. 175).

RETORTS. Murdoch's first retorts were of cast iron, placed vertically in a furnace (Fig. 44), but as it was inconvenient to charge them Murdoch introduced inclined retorts (Fig. 45), which he changed later into horizontal retorts of cast iron (Fig. 46).

[1] Wright analysed the gas for three different periods, starting from the beginning of the distillation, the results being:

	After 40 minutes Per cent.	After three hours. Per cent.	After six hours Per cent.
H_2S	0·4	0·78	0·38
CO_2	2·08	1·34	0·59
CO	4·52	6·73	7·52
CH_4	56·46	37·46	14·61
H	25·36	48·36	91·04 (?)
Heavy hydrocarbons	8·51	3·13	2·78
N	2·37	2·20	2·18

[2] By passing ordinary gas into a retort filled with coke at 1200° or a higher temperature, a new gas, deprived of heavy hydrocarbons, oxygen, and carbon dioxide, very poor in methane (6 per cent.), rather richer in carbon monoxide (7 to 8 per cent.) and very rich in hydrogen (up to 84 per cent.) is obtained. This new gas can be used for aeronautical purposes its specific gravity being about 0·23 (*Continental Gas Gesellschaft*, Dessau, 1910).

In 1820 J. Grafton suggested the use of horizontal retorts of fireclay, since these resist heat better, cost less and last longer. The most convenient form was that with a ⌓-shaped or elliptical section (Fig. 47), and the most suitable dimensions for these horizontal retorts were found to be: width of the mouth, 43–53 cm., height at the middle, 31–38 cm., and length, 2–3 metres. One end was closed and the mouth was swelled at the edge,

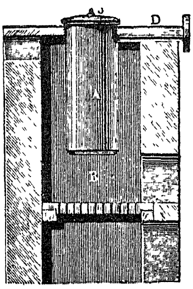


Fig. 44.

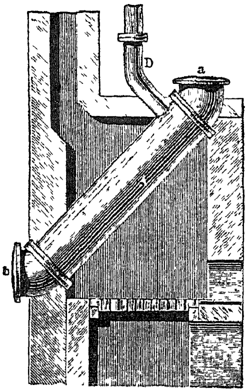


Fig. 45.

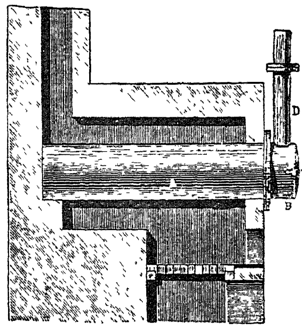


Fig. 46.

which carried screws serving to fix the metal cover fitted with the delivery tube. These retorts were charged, according to their capacity, with 100–200 kilos of coal, broken into uniform lumps. Various mechanical connections were devised to allow of the retort being charged and discharged rapidly and with the least expense for hand labour, and one of the best arrangements, with a battery of retorts placed in regenerator furnaces (*see* vol. i, p. 500), is that shown in Fig. 48. However, since 1890 it has become general in the principal European towns to use inclined retorts of elliptical section, which were suggested anew by Coze and are furnished with two mouths projecting from the two ends of the furnace (double-ended or "through" retorts). When these are inclined at an angle of 32° and are charged automatically from above, the coal distributes itself in a layer of uniform depth along the whole of the retort (Fig. 49). The gas-discharge tube is inserted at the lower mouth, which at the end of the operation is opened, the coke, while still hot, being completely and immediately discharged into an iron truck or on to a moving endless perforated band, the pieces of coke remaining alight being sprinkled with water before being discharged on to the coke ground. Similar retorts are used with elliptical mouths; the upper one is rather larger (63 cm. × 35 cm.) than the lower (57 cm. × 30 cm.), and the length is about 3·8 metres. At the present day they vary from this length up to 6 metres.

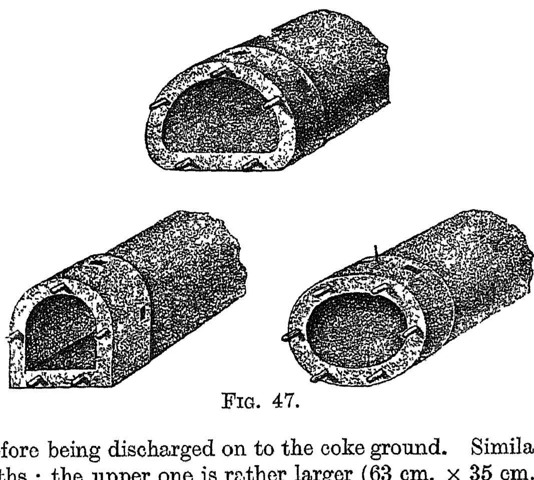


Fig. 47.

The advantages of this system are shown by the following results, which refer to three batteries of fourteen (1) inclined and (2) horizontal retorts:

	Inclined	Horizontal
Duration of the distillation . . .	3 hours	$4\frac{1}{2}$ hours
Charge per retort	165 kilos	152 kilos
Number of charges per 8 hours . .	112	72
Total coal distilled in 8 hours . . .	18,500 kilos	11,000 kilos
Cost of labour per 1000 kilos of coal . .	10 pence	18 pence

The *pressure* in the interior of the retorts should be carefully regulated, since if it becomes too great, escape of the light gases and vapours readily occurs and the development of vapours and gases is slackened, the hydrocarbons, which remain for a long time in contact with the red-hot walls of the retort, undergoing further decomposition with deposition of graphite on the walls and liberation of hydrogen. In order to avoid these inconveniences the retorts are to-day put in indirect communication with aspirators or pressure regulators placed beyond the washing apparatus (scrubbers, &c.).

The layer of coal in the retort should not be too deep, as otherwise the gases given off are decomposed on contact with the upper layers of hot coke.

With the view of avoiding decomposition of the more luminous gases which are evolved principally at the beginning of the distillation, Bentrup (1903) proposed passing a continuous current of *water-gas* (*see* vol. i, pp. 392, 393) into the retort to remove these products rapidly from contact with the hot walls of the retort ; the water-gas is produced in an adjacent retort also containing red-hot coke.

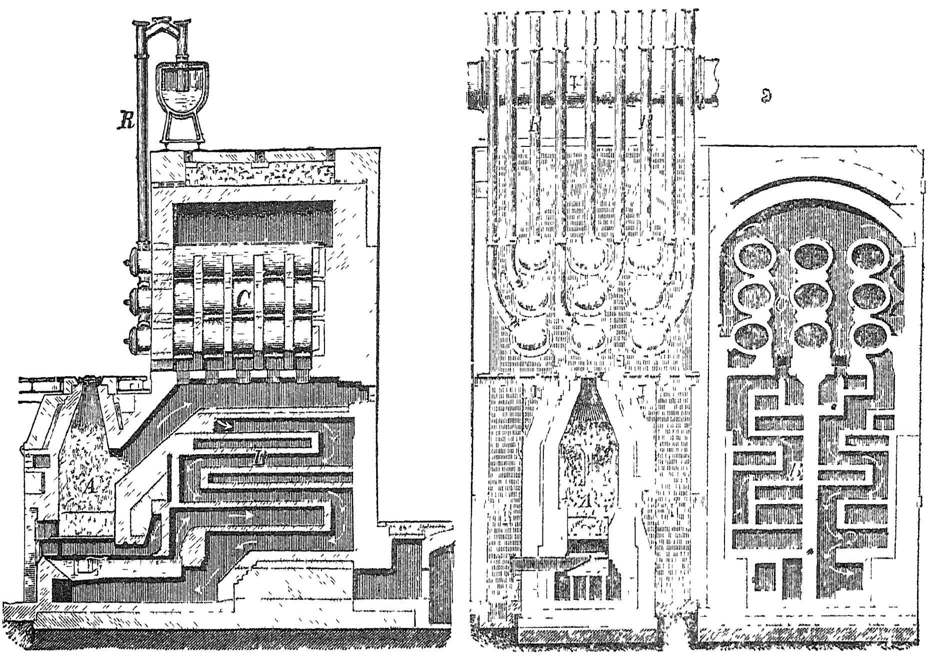


FIG. 48.

As often happens in other fields of work, so also in the industries a return to older methods often offers advantages. Thus it appears at the present time that the vertical retorts again brought into use by Settle and Padfield are destined to supplant the inclined ones. In 1905 Dr. J. Bueb made works experiments with a battery of ten retorts, 4 metres in length, placed vertically in a furnace and provided with an upper aperture for charging and a lower one for discharging (that is, the furnace surrounds only the external vertical surface of the retort, which is heated by hot gases circulating through numerous channels, as shown in Fig. 50). In this way a larger charge (up to 500 kilos) is used, the luminous gases are not decomposed and the yield of gas is higher, as the temperature of the retort reaches 1300–1400° C. ; at the same time very little naphthalene is produced, the inconvenience caused by depositions of naphthalene in the cold parts of the pipes being thus avoided. In addition, the yield of ammonia is increased by 35 per cent., the separation of the tar is facilitated and the cost of labour diminished ; a less amount of a harder coke is obtained, and the quantity of tar is considerably decreased, while the production of gas is increased (Ger. Pat. 155,742).

Fig. 50 shows a double battery of Bueb vertical retorts, 4 metres high and slightly conical in shape, the wider mouth at the bottom. By means of the elevator *A* the coal is introduced into the hopper *B C*, whence it passes into the movable scoops *D*, which

carry it to the retorts. At the end of the distillation (which lasts 7–8 hours) the coke is discharged into the metal hopper, *F*, and thence into the channel, *G*, where a band running on rollers carries the spent coke to the store. The gas issues at the top of the retort and by the tubes, *E*, passes into the hydraulic main, *I*, and so into the piping, *L*; the tar and the ammonia liquors are discharged from the hydraulic main into the tube, *M*, leading to the depositing tank.

In order to increase the yield of gas by 10–15 per cent. it has recently been proposed to utilise the high temperature of the coke (1400° C.) remaining in the retorts at the end of the distillation to produce a certain quantity of water-gas by passing a current of steam in at the bottom of the retort for an hour. It cannot, however, be denied that by this *wet process* the proportion of carbon monoxide in the gas is increased. In any case total yields of 360 cu. metres of gas per 1000 kilos of coal have been obtained in this way.

The economy in labour effected by this retort is very great, and it is calculated that, whilst with horizontal retorts every workman produces about 1600 cu. metres of gas per day, with the vertical retorts the amount reaches 7000 cu. metres.

From 1906 to 1910 furnaces with 507 batteries of 5500 vertical retorts, representing a total daily production of 2,200,000 cu. metres of gas, have been manufactured by one single firm at Dessau (for Berlin, Cologne, Zurich, Trieste, Geneva, &c.).

In the working of these vertical retorts, which do indeed represent a marked advance on the Coze inclined retort, certain disadvantages have been observed, the coke formed being harder than the ordinary and not so well suited for domestic purposes; whilst the gas-discharge tubes soon become obstructed with tarry matters so that they require cleaning every 3–4 days; distillation with steam during the last phase of the heating relieves this inconvenience to some extent. By some the production of water-gas as described above is not regarded as advantageous, the same quantity of water-gas being obtainable more economically with special plant.

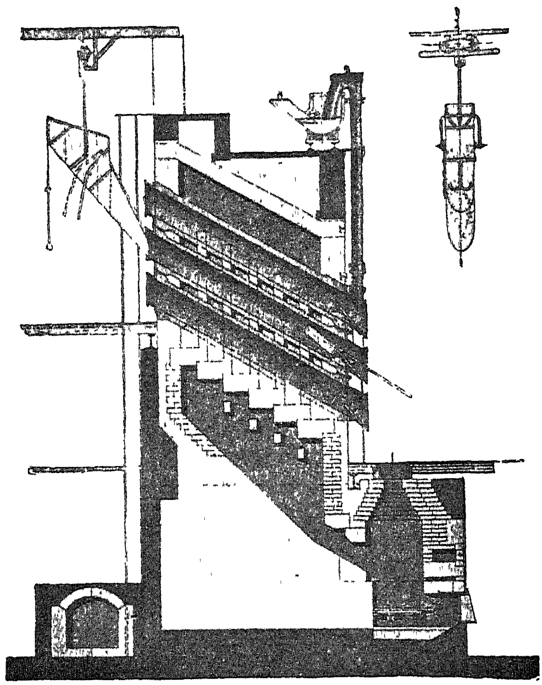


FIG. 49.

A further and more recent modification consists in the use of *chamber furnaces* (similar to those for making metallurgical coke, *see* vol. i, p. 367).

At Monaco in 1906 and at Vienna in 1909 *inclined chamber furnaces* were employed (Kopper system, Fig. 51). Coal from the hopper, 2, passes down an inclined plane and fills the chamber, 5; the gas is led into the trough, 1, the coke is discharged, by opening the large lower door with a crane, on to an inclined plane and so to the chain transporter, 6, and the gasogen, 8, passes the gas to the dust-chamber, 7, and then to the ascension pipes under the chambers; 9 shows another battery of inclined chambers. With chamber furnaces a better gas is obtained with a less expensive plant and a decided economy in labour, the daily yield of gas per workman reaching 9000 cu. metres. A plant of this kind was finished in 1910 at Padua.

With horizontal or inclined retorts the coal is heated for 4–6 hours; with vertical ones, 12 hours; and with chamber furnaces, 24 hours.

FURNACES. Retorts were first of all heated by direct flame, but in this way the heat is inefficiently utilised; then indirect heating by flues, just as for steam boilers, was tried, but the nearer retorts wore out very rapidly, so that later several retorts were placed

in one furnace in direct contact with the hot gases, these being so interrupted and deviated that the surfaces of all the retorts were uniformly heated (Fig. 48).

At the present time the use of the *regenerator gas furnace* (*gasogen, see* vol. i, p. 501) has become general, coke (usually waste) being employed, and, in countries where there is

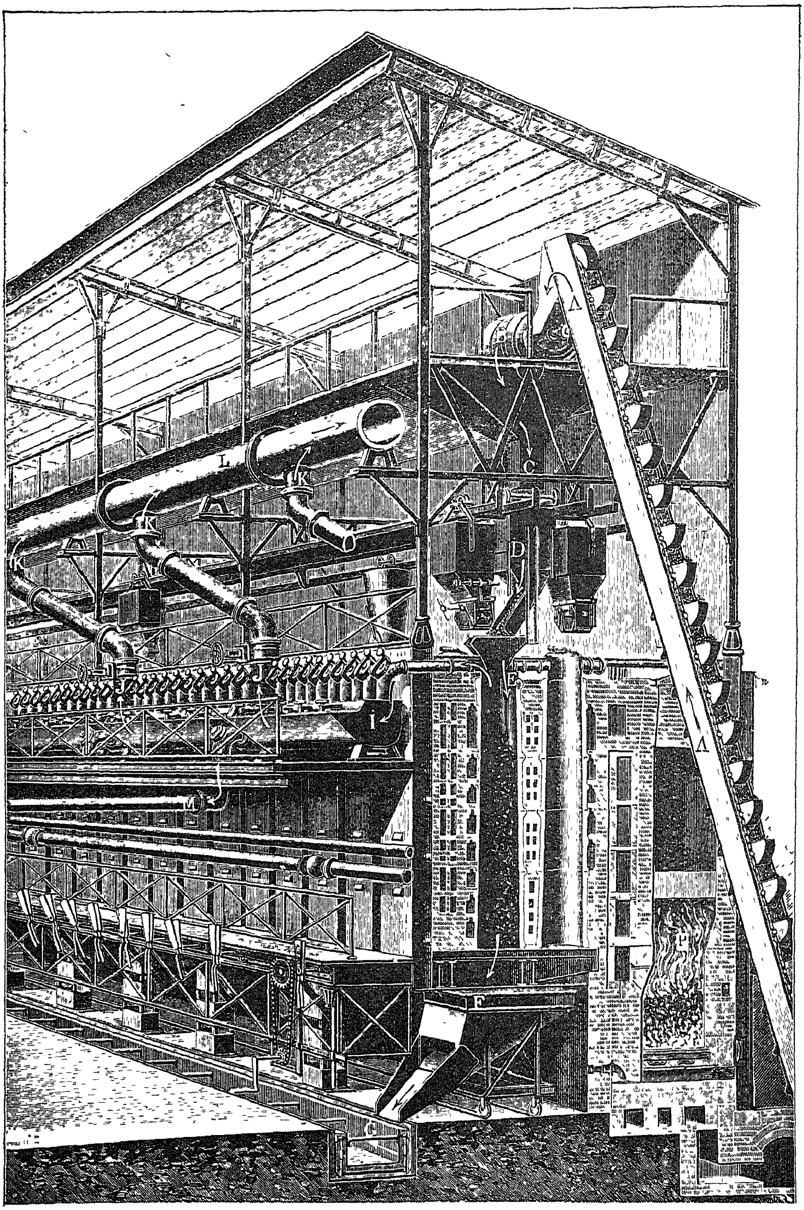


FIG. 50.

little demand for tar, the latter being used as fuel by injection into suitable furnaces. The coke used to heat the furnaces represents about 25 per cent. or 30 per cent. of the total amount produced. In some works (*e.g.* at Turin since 1909) the heating of the furnaces is profitably effected by 9–10 per cent. of tar (on the weight of coal distilled), burnt in special gasogens.

The wear of the furnaces and retorts is considerable, and their cost is calculated as

annual expenditure rather than as cost of plant, since they are sometimes remade or renovated twice a year.

PURIFICATION OF GAS. The crude products obtained directly from the carbonisation of bituminous coal cannot be used immediately for lighting and other purposes. The gas issues from the retorts at very high temperatures (up to 250°), and it is evident that, as it gradually cools, various products separate, first of all those which are solid or liquid at ordinary temperatures. It is necessary to remove the tar, naphthalene, ammonia liquor, and the cyanogen and sulphur compounds by means of the following apparatus.

HYDRAULIC MAIN. This is a wide circular or semi-circular pipe (diameter, 30–60 cm.) of sheet-iron or cast-iron (Fig. 48 *V*), containing water and tar, and placed above the retorts so that the ascension pipes, *R* (12–18 cm. in diameter) from one battery of retorts dip into it, these pipes starting from the lower parts of the retorts and carrying off all the hot gas developed. The tubes, *R*, are sealed hydraulically by dipping into water in the hydraulic main, in which most of the tar and a little of the ammoniacal liquor condense. The hydraulic main falls slightly towards one end so as to facilitate flow of the tar to the store-tanks, in which it gradually becomes almost entirely separated from the ammonia liquors, being sold to the tar-distiller with a content of not more than 5 per cent. of water at a price of about 17 pence per cwt. (lire 3,50 per quintal).

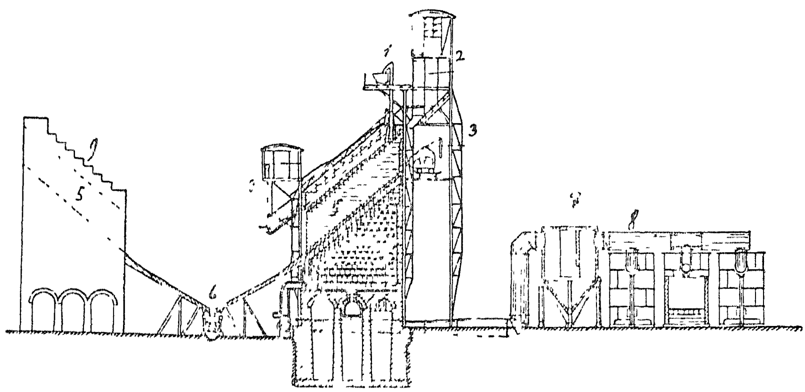


FIG. 51.

The still very impure gas, holding in suspension large numbers of tar drops—which render difficult the condensation of the naphthalene—and having a temperature of 60–100° C. is gradually cooled to 12–15° C. by causing it to traverse a large iron pipe passing round inside the whole of the works and cooled by the air ; the gas then reaches a condenser formed either of a battery of long iron tubes (Fig. 52) sprayed outside with water, or of a series of three or four double-jacketed cylinders cooled inside and outside by the air, the gas passing into the jacket (Fig. 53) ; or the gas may be circulated round a number of narrow tubes through which passes a continuous stream of cold water (Fig. 54). The cooling thus effected is gradual, and the separation of the naphthalene and tar is more complete, while there is no danger of stoppages from the naphthalene ; in winter the gas enters the cooler at 50–60° C. and leaves at 5–10° C., while in summer it enters at 60–70° C. and emerges at 30–35° C. At the bottom of these tubes is found a deposit of tar—which is discharged into tanks—and of ammonia liquors at 7–8° Bé. The consumption of water in these coolers is from 3–4 cu. metres per 24 hours per 1000 cu. metres of gas.

If an obstruction of naphthalene occurs at any point, the pressure—indicated by manometers placed along the tubes—shows an increase at that point.

The gas issuing from the condensers still contains suspended tar, which it is necessary to separate. To this end serves Audouin and Pelouze's tar-separator, shown in Fig. 55. The gas passes along the tube *B*, which opens into a perforated double-walled bell, *D*, the pressure in which is regulated by a compensating weight and pulley, *G*. The bell is partially sealed hydraulically and rises more or less, leaving open a greater or less number of apertures, according to the pressure of the gas. The gas is thus subjected to a kind

of filtration through small orifices, the fine drops of tar being condensed into larger drops, which separate and collect in *E*, whence the excess is run off at *F*. The gas thus purified from tar passes by the tube *C* to the ammonia-condensing apparatus. The tar-separator should not be kept too cold (12–15° C.)

NAPHTHALENE SEPARATORS. Naphthalene is a product of the condensation by heat of the heavy hydrocarbons of the gas. It is difficult to imagine how pertinaciously gas carries through all the purifying operations considerable quantities of naphthalene suspended in it, and how slowly this naphthalene is deposited in town mains, ultimately stopping them and causing great inconvenience and expense to consumers and manufacturers.

In 1899 Bueb, on the basis of former experiments of Young and Glover, succeeded in avoiding this trouble to a great extent by passing the gas (first washed with water in the "Standard" washer-scrubber to separate the ammonia) into a drum similar to the "Standard" (*see below*), but with three independent chambers in which the gas is washed with anthracene oil of medium density (prepared by the distillation of tar and having a b.pt. 350–400° C.), which dissolves

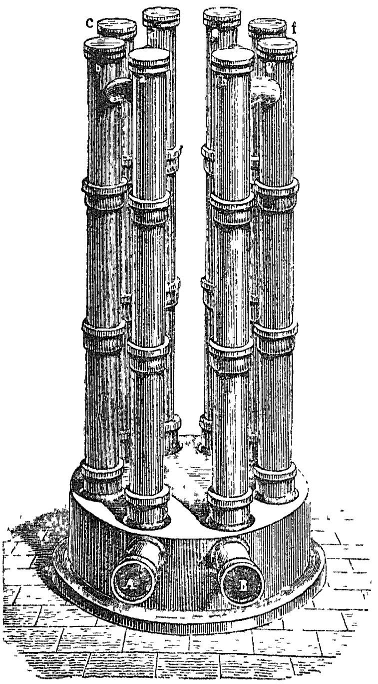


FIG. 52.

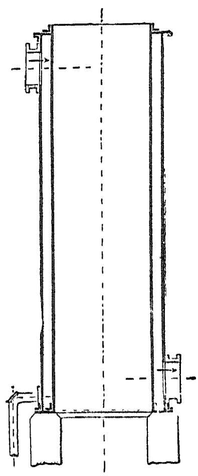


FIG. 53.

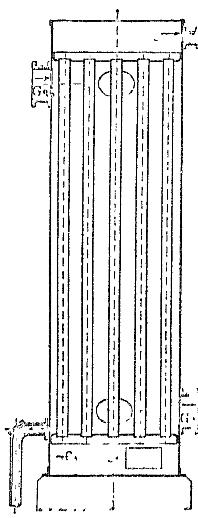


FIG. 54.

and fixes almost all the naphthalene. When the oil of the first chamber is saturated it is removed, and that of the second chamber passes into the first and that of the third into the second; the third chamber is charged with fresh oil, containing 4 per cent. of benzene in order to avoid loss of light-giving products from the gas. The anthracene oil, saturated with naphthalene (25 per cent.) can be utilised as such, or mixed with ordinary tar.

According to U.S. Pat. 968,509 of 1910, naphthalene can be separated by bubbling the gas through an aqueous solution of picric acid, this giving rise to an insoluble naphthalene picrate, from which the naphthalene can be distilled by means of steam, the picric acid being left.

SEPARATION OF AMMONIA. The washing of the gas for the purpose of removing the ammonia may be effected by ordinary water, which has a great affinity for ammonia, or by the dilute ammonia liquors from the hydraulic main (1–2° Bé.), but not with that from the condenser, which is too concentrated (7–8° Bé.). The most common form of apparatus used for this washing is the *scrubber* or, better still, the "Standard" washer-scrubber.

SCRUBBERS are usually formed of a series of coke-towers through which water trickles (Fig. 56). The gas that enters the bottom of the first tower is washed with dilute ammonia, condensed in succeeding towers, and when it reaches the last tower it is washed

with pure water which dissolves the last traces of ammonia and can be used subsequently for the first tower, from the bottom of which it is carried off, rich in ammonia, by small syphons. These towers, which are of cast-iron sheets, are joined in twos or threes in such a way that the gas is conducted from the top of the first tower to the bottom of the second, and so on. The interior may be fitted simply with water pulverisers, or it may be filled with coke, chips of wood, broken bricks, or, what are more efficient, vertical bundles of sticks, or of corrugated and toothed iron sheets.

Scrubbers are 1–3 metres in diameter and 4–20 metres in height. A maximum production of 1000 cu. metres of gas per 24 hours requires 5–6 cu. metres of scrubber, the gas taking 8–10 minutes to pass through. Before entering the scrubber the gas contains 200–400 grms. of ammonia per 100 cu. metres, whilst afterwards this volume contain only 1–10 grms.

The "**STANDARD**" washer-scrubber consists of a large horizontal fixed cylinder of iron-plate, divided into seven chambers (Fig. 57). This cylinder is traversed by a rotatable

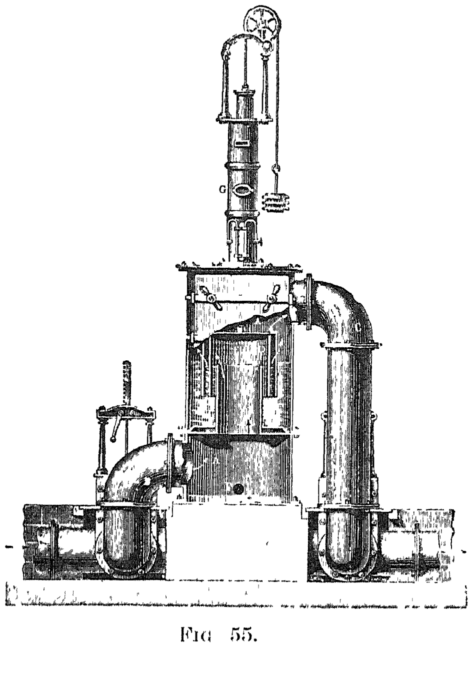


FIG 55.

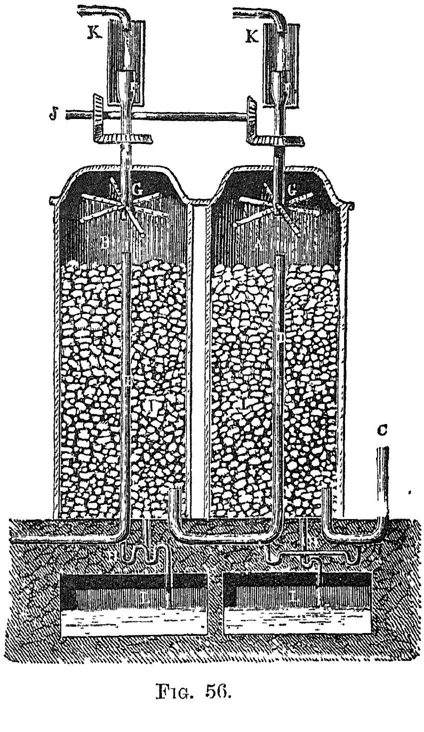


FIG. 56.

axis carrying seven paddles of almost the same diameter as the chambers and each consisting of two large metal plates to which are fixed the ends of superposed wooden laths with spaces, not exactly superposed, between (Fig. 58). These paddles rotate with the axis and dip into water which fills the chambers to about one-third of the height of the cylinder. The pure water enters chamber VII at *a* and passes from chamber to chamber until it reaches the first, the walls separating the chambers being successively lower. The gas to be purified moves in the opposite direction, entering chamber I, and passing between all the laths of the paddle from the centre to the periphery, then descending to the centre of the next paddle in chamber II as shown by the arrows, 4 and 5, again issuing at the periphery, passing into chamber III, and so on. In this way the gas is perfectly washed and loses also part of its CO_2 and H_2S. The water leaves chamber I with a density of 7–8° Bé.

At Monaco the ammonia is eliminated in the dry way by passing the gas over superphosphate, which fixes it and then serves as an excellent fertiliser (with 7–8 per cent. of nitrogen): 1000 kilos of superphosphate are sufficient to purify 32,000 cu. metres of gas (with 3 per cent. of NH_3), the small quantity of thiocyanate (0·5–2·5 per cent.) which it contains having no injurious action on plants. N. Caro (U.S. Pat. 952,560, March 22,

1910) cools the gas from coke manufacture to 20° and then passes it through a solution of ammonium sulphate of 29–35° Bé. containing 5 per cent. of free sulphuric acid; ammonium sulphate gradually crystallises out and the gas passes off free from ammonia. Generally, however, ammoniacal liquors are distilled with lime and the ammonia fixed with sulphuric acid (*see* vol. i, p. 323). Every ton of coal carbonised yields 10–12 kilos of commercial ammonium sulphate

FINAL AND COMPLETE PURIFICATION OF GAS. After the ammonia, the following gases must be removed: H_2S, CO_2, HCN, CS_2, thiocyanates, sulphur derivatives of hydrocarbons, &c. This is especially important with H_2S and other sulphur compounds (about 1–1·5 per cent. by volume of the crude gas), since they partly burn, forming SO_2, and partly escape unaltered from the gas-jets, decorations, metal-work, and paintings being discoloured; also the poisonous properties of these compounds are considerable, the crude gas containing 0·1–0·25 per cent. by volume of hydrocyanic acid. The test employed by large consumers to detect hydrogen sulphide is very rigorous and is made with lead acetate paper, which blackens on prolonged exposure to impure gas.

The final purification of gas has been in use ever since the beginning of the industry. In 1806 Clegg purified gas partially by passing it through milk of lime, but such large

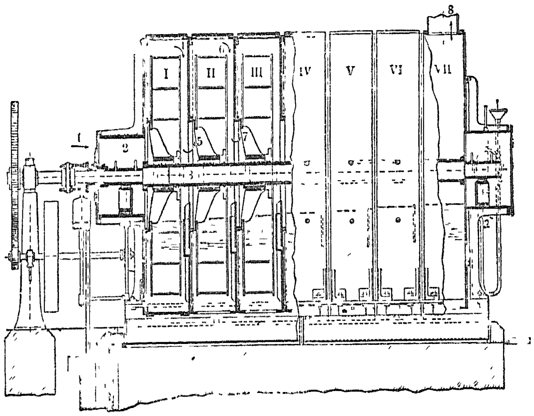


FIG. 57.

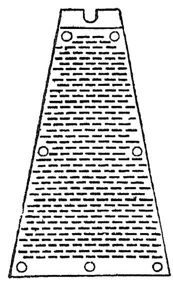


FIG. 58.

volumes of liquid were required that their preparation was difficult and the purification was not complete. He then proposed the use of powdered slaked lime, which fixes carbon dioxide, as well as many sulphur compounds, forming calcium sulphydroxide, OH·Ca·SH; but if much CO_2 is present the sulphydroxide is decomposed and SH_2 regenerated. In 1840 Mallet suggested the use of manganese oxide, which fixes H_2S more readily, but this method did not give good results.

At the present time use is largely made of the so-called Laming mixture, which is prepared by mixing 160 parts of lime, 180 of sawdust and 30 of ferrous sulphate dissolved in scarcely sufficient water to moisten the mass; it is kept turned over for some days in the air, until it becomes brown owing to the conversion of the ferrous sulphate into ferrous hydroxide and then ferric hydroxide, calcium sulphate being formed at the same time. The latter fixes the ammonium salts (such as have not been already separated), while the ferric hydroxide fixes hydrogen and other sulphides: $2Fe(OH)_3 + 3H_2S = 6H_2O + F_2S_3$ (iron sesquisulphide), and also forms iron thiocyanate from hydrocyanic acid (*i.e.* from ammonium cyanide) and thiocyanates, the excess of lime removing the carbon dioxide.

The whole of the iron present does not take part in these reactions, but when the mixture is exhausted it can be regenerated by further exposure and turning in the air for two or three days, the whole of the sulphur being liberated:

$$Fe_2S_3 + 3O + 3H_2O = 2Fe(OH)_3 + 3S.$$

The mass can be thus revivified and used again some ten or more times, after which it is rejected. But this product contains 35–50 per cent. of free sulphur, 10–15 per cent. of Prussian blue, 1–4 per cent. of ammonium thiocyanate and 1–4 per cent. of ammonium sulphate, and nowadays the free sulphur is often extracted by carbon disulphide, while

from the residue cyanides and ferrocyanides can be obtained ; or the mass is first extracted with water to obtain the cyanides and the ammonium sulphate, the dried residue being used in place of pyrites in the manufacture of sulphuric acid (*see* vol. i, p. 650) [1]

As will, however, be seen, the lime takes no part in the separation of the hydrogen sulphide (but only in the fixation of the CO_2), so that, in the last few years, Laming mixture has been replaced by hydrated ferric oxide (minerals such as limonite, &c.) mixed with a little lime and sawdust ; by using natural oxide of iron alone, the reaction becomes very energetic, the mass being sometimes almost ignited. These mixtures give good results and are placed on the market under various names : Deicke mixture with 66 per cent. Fe_2O_3 and Lux mixture with 51 per cent. Fe_2O_3. They are made by mixing the powdered iron residues from the working of bauxite with soda and fusing in a furnace, the silicates which have become soluble being then extracted by water and the remaining ferric hydroxide mixed with double its volume of sawdust : 1 cu. metre of this "Lux" mixture, at an initial cost at the Ludwigshafen factory of about 15*s*. per ton, purifies more than 10,000 cu. metres of gas, whilst natural Silesian ferric oxide costs 8–12*s*. per ton.

The purifying mixture is arranged in several layers, all of which are traversed by the gas (Fig. 59). The cover to the chamber is water-sealed (Fig. 60), and can be easily raised by means of a crane when the mass is to be removed for regeneration. It is simpler to

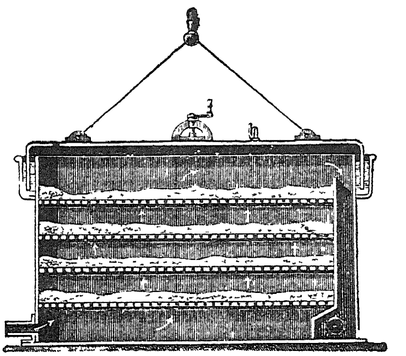


Fig. 59.

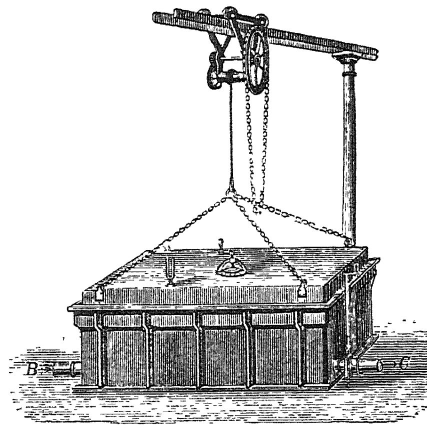


Fig. 60.

use a single layer of the mass 50–60 cm. deep, the gas being introduced at a greater pressure ; it is then easier to discharge the exhausted mass through an aperture in the base of the reservoir.[2] At the present day the costly labour required for the regeneration is avoided by not emptying the reservoir, a rapid current of air or oxygen being passed through for several hours, this operation being rapid, complete and economical ; in some works, however, the mass is kept always oxidised by mixing about 2 per cent. of air with the gas before passing it into the chamber.

[1] The cyanogen compounds of the crude gas which are formed from ammonia by the action of heat and cause corrosion of ironwork are best separated in the *wet* way by Bueb's process (Ger. Pat 122,280, May 1900), in which, before being freed from ammonia, the gas is passed into a kind of "Standard" containing ammonia and a ferrous sulphate solution of 20° Bé. By this means, ferrous sulphide first gradually separates [$FeSO_4 + (NH_4)_2S = FeS + (NH_4)_2SO_4$], and is then slowly converted, under the action of ammonia and hydrocyanic acid, into an insoluble mass composed of ammonium ferrocyanide, $(NH_4)_4FeCy_6$ and of a ferrous ammonium ferrocyanide, $(NH_4)_6Fe(FeCy_6)_2$. This sludge, which contains all the cyanides, corresponding in amount with 15 to 20 per cent. of crystallised potassium ferrocyanide, is heated to render insoluble the small quantity of cyanide still undissolved and to drive off ammonium carbonate, and is then passed to filter-presses; the filtrate is utilised for the extraction of ammonium sulphate, while the cyanide residue is heated with lime to give ammonia and calcium ferrocyanide, a solution of the latter yielding pure sodium ferrocyanide when treated with sodium carbonate. This process has given satisfactory results in the Turin gasworks and many others in Europe, but is already beginning to lose its importance, owing to the discovery of new synthetical methods of preparing potassium cyanide (vol. i., p. 435).

[2] This exhausted mass is often utilised for the sulphur it contains, while in many other cases the cyanides, thiocyanates, ferrocyanides, &c., are extracted (*see* vol. i, p. 650) ; it is also sometimes used on roads as a weed-killer—cyanides having a poisonous action on plants—and, finally, it has been proposed as a nitrogenous fertiliser (it contains on the average 5–6 per cent of nitrogen, one-tenth of which is in the form of ammonia and the rest as cyanide), but it must be spread on the naked land two or three months before sowing takes place, as it takes time to decompose and become innocuous to vegetation.

After purification the gas passes through large meters to the gasometers, after traversing a glass bell-jar in which is suspended a strip of moist lead acetate paper for the detection of H_2S.

In order to diminish the quantity of carbon monoxide in gas, L. Vignon (1911) proposes to heat it over lime and with steam, by which means non-poisonous hydrocarbons are formed.

EXHAUSTERS. To regulate the pressure of the gas in the retorts and other parts of the plant, exhausters are placed between the condensers and the tar separators, or even after the scrubbers. Sometimes a bell-aspirator is used, consisting of a bell immersed in water and capable of being raised and lowered mechanically, and thus, by means of suitable valves in the lid, of acting both as exhauster and as compressor. There are also piston exhausters, others similar to exhaustion pumps working by eccentrically moving blades (Beale type), &c. The so-called Körting injectors, which make use of steam-jets, are also used as exhausters.

PRESSURE REGULATORS. Since the development of gas cannot be regulated in the retorts, whilst the working of the exhausters is uniform, there may at certain times be an excess pressure generated, especially if the exhausters cease working owing to damage. Hence, so-called *pressure regulators* are employed.

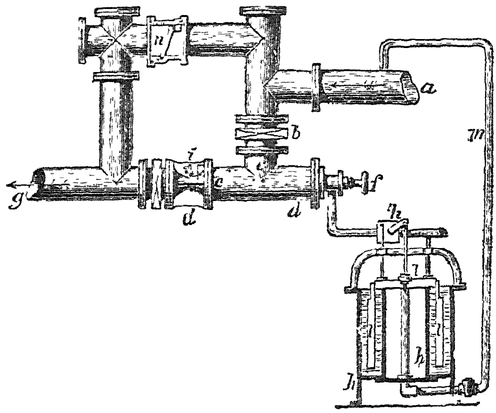


FIG. 61.

To give an idea of one of these simple and ingenious devices, it is shown in Fig. 61 how this regulator is combined with a Körting steam exhauster: *d* is the exhauster, which receives steam from a valved tube, *b*, connected with a bell, *l*, with a water-seal. The gas from the tube *a* passes through the exhauster to the pipe *g*. If an excessive pressure develops in the main *a*, the gas, by means of the tube *m*, raises the bell *l*, which in its turn effects a wider opening of the steam-valve and so increases the exhaustion. If the pressure exceeds a certain limiting value, a spring valve or partition in *n* opens automatically, and the gas discharges also by *n* into the pipe *g*.

GASOMETERS. These are formed of large sheet-iron bells fitting one in the other and forming a perfect water-seal when they are inverted in a brick and cement reservoir of water. To economise water, the reservoir is partially filled up by a brickwork cone (termed the "dumpling"), starting from the periphery at the base and rising towards the centre, as shown in Fig. 62; the gas exit and entry pipes project a little above the surface of the liquid. At a certain point (not shown in the figure) these two pipes can be put into direct communication, so that, in case of accident to the gasometer, the gas can still be led to the mains without interrupting the work.

To economise in the number and size of the reservoirs and to have gasometers of considerable capacity, so-called *telescopic gas-holders* are now used. These consist of several concentric bells (five or six), of which only the smallest is covered, whilst the others are caught up peripherally during the rising (or filling with gas), forming a water-seal all round, as shown in Fig. 63. In order that the bells may rise centrally they are furnished outside with pulleys running along vertical iron guides. The pressure of gas in the gasometer can be calculated from the weight of the bell outside the water, together with the surface and diameter of the bell itself.

The pressure in the gasometer or mains can be registered automatically by placing them in communication with an automatic pressure-measure like that shown in Fig. 64. In this the gas raises or lowers a bell fitted with an index which registers the different pressures during the day on a paper wound round a cylinder rotated once in 24 hours by clockwork.

There are other forms of pressure indicators, but the above, although old (in principle), is still largely used, being simple and exact.

In order to avoid the serious consequences contingent on a gasometer reservoir cracking or leaking, iron reservoirs built above ground are preferred to-day, the slightest escape being then observable and remediable at any moment. Such a *suspended telescopic gasometer* is shown in Fig. 63.

To meet the enormous daily consumption of gas in large cities more and more capacious gas-holders are required—sufficient to contain 3 or 4 days' supply and so avoid the inconveniences of an interruption of work (from damage, stoppages, &c.). In Milan, before 1908, the largest of the gasometers (measuring altogether 150,000 cu. metres) had a capacity of 26,000 cu. metres; after 1908, at the Bovisa (Milan) works a new one was brought into use which holds 80,000 cu. metres and cost little less than £40,000. The firm of Krupps constructed for their own works a gasometer holding 37,000 cu. metres; the largest at Berlin contains 80,000 cu. metres; that of Chicago 120,000 cu. metres; and the last built at New York has a cement reservoir and a capacity of 500,000 cu. metres; in London in 1888 one was built holding 230,000 cu. metres, and in 1892 another with six bells, containing 345,000 cu. metres and having a diameter at the base of 95 metres. Naturally these gas-holders represent large amounts of capital, the cost even for capacities of 30,000–40,000 cu. metres being tens of thousands of pounds. Fig. 65 shows diagrammatically the arrangement of a gasworks in the middle of the nineteenth century.

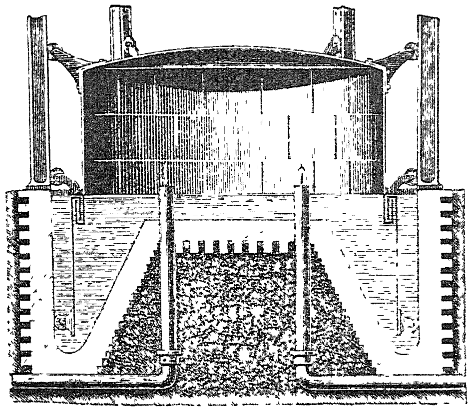


FIG. 62.

PRESSURE REGULATORS FOR CONSUMERS. In order that consumers may have a uniform pressure in their pipes and obtain regular, non-oscillating flames with a normal consumption of gas, it is necessary to use pressure regulators where the principal mains leave the works, these regulating the pressure automatically even when the consumption is at its maximum or minimum. Since gas is lighter than air, the pressure is regulated more easily and the flow facilitated by constructing the works at the lowest point of the town. In the gas-holder the pressure is usually 15 cm. of water, whilst in the mains it is about 2 cm.

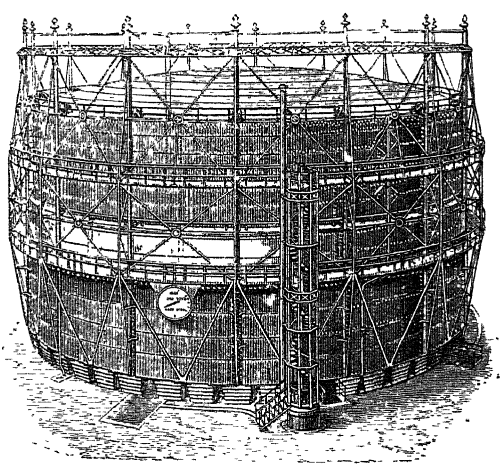


FIG. 63.

A regulator as ingenious as it is simple was devised by Clegg and is in general use at the present time (Fig. 66). In a metal cylinder, *a*, filled with water, a bell, *b*, can be raised or lowered according as the gas supplied at *f* has a greater or less pressure. The pressure in the bell can be varied by altering the size of the aperture in tube *f* by which the gas is admitted. The orifice *i* at the upper end of *f* can, indeed, be closed to a greater or less extent by a metal cone, *e*, attached by a chain to the bell, with which it rises if the pressure is excessive—thus diminishing *i* and hence the pressure in the bell—or falls if the pressure diminishes too much, more gas then entering through *i* and the normal pressure being thus re-established. This normal pressure can be fixed according to the needs of any particular time, by placing on the bell weights, *d*, calculated to give the required

pressure. By means of this simple regulator the gas issues from h at a constant pressure and can be immediately passed into the mains.

In general, however, the pressure is not the same in all the mains, but diminishes as the distance from the works increases. But it is not advisable to have the pressure too high, since the losses due to unavoidable leaks in the pipes are greater the higher the pressure, and the latter is usually maintained at 15–20 mm. of water at the points most remote from the works.

In order to render the distribution of the gas to considerable distances more economical, attempts have been made to employ a pressure of 1–1·5 atmos. on the gas, the latter being preferably from vertical retorts and as free as possible from naphthalene.

GAS-METERS. These are used to measure the gas in factories and private houses, since nowadays payment is according to the volume consumed and not according to the number of burners, as was once the custom. Dry meters have disappeared almost everywhere, general use being made of the water meters devised by Clegg and by Malam, and since improved so that they are now perfect gas-measurers. The principle on which their working is based is shown clearly by Fig. 67, representing an old form of the Malam meter. A cylindrical chest, X, half-filled with water, contains a drum rotatable about a horizontal axis and divided into four chambers, A, B, C, and D, communicating at the centre by means of the narrow slits b, and opening into the periphery at X by the slits c. The gas is led by the tube a into the central part of the drum and, in the position shown in the figure, communicates only with the slit b of the chamber D; the latter is thus slowly filled with gas (which has a slight pressure), the drum being thereby raised and water caused to escape from c. Thus the chamber D becomes filled with gas in the position occupied by C, which has allowed its gas to escape gradually, the rotation indicated by the arrow having caused it to fill with water through the corresponding slit, b. Subsequently the gas fills the next chamber, A, which displaces D, and so on. The gas passing through this apparatus proceeds along the tube K to the consumer's burners. If all the taps are turned off, the drum cannot allow the gas to escape from it, and hence does not turn. The chambers have definite volumes, and if the axis of the drum is connected with a suitable magnifying apparatus the number of turns of the drum and consequently the volume of gas traversing it can be measured.

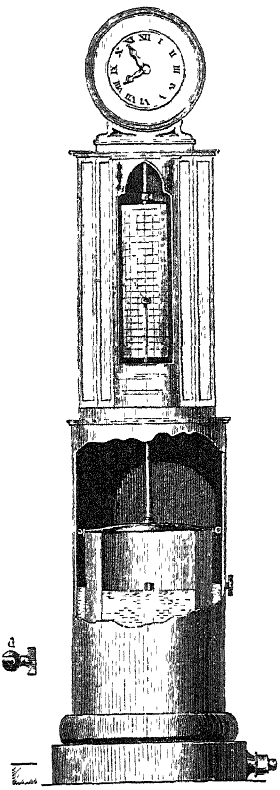


FIG. 64.

This apparatus exhibits many structural defects which cause inaccurate measurements, and are now avoided by the meter shown in Figs. 69, 70, and 71. Here the drum has transverse walls which are inclined and not parallel to the axis (Fig. 68, V, W), so that the filling with the gas or water and the discharge take place gradually and do not cause oscillation of the flame. The gas enters by the tube l into the division k (Figs. 69 and 70) and passes into E through the orifice i, regulated by a floating valve, h. Thence the gas goes to the anti-chamber, B, by way of the elbow-tube, $n\,x$, opening above the level, W, of the water. The aperture, o, connecting the tube, x, with the anti-chamber is large enough to admit of the passage of the axis of the drum, but remains closed owing to the level of the water being above it. As the slits of the drum gradually present themselves, the gas enters successively the chamber of the drum from one side and issues at the other into the outer casing, A, then passing through the tube g to the gaspipes. Water (or better, a mixture of water and glycerine, which does not freeze) is introduced by the opening V, the level of the liquid being fixed by the tube n, so that the flow of gas through the valve i, is regulated; the excess of water is discharged by the tube n and passes into the reservoir, m, thence by the tube t to S, the orifice, u, of which is left open while the water is being added.

The axis of the rotating drum has, at one end, a continuous screw, *a* (Fig. 71), which moves a toothed wheel, *a*; the latter, by means of the axle, *e*, produces rotation of a clockwork arrangement in *F*, so constructed that one wheel indicates litres and tens of litres, another cubic metres, a third tens of cubic metres, and a fourth hundreds of cubic metres.

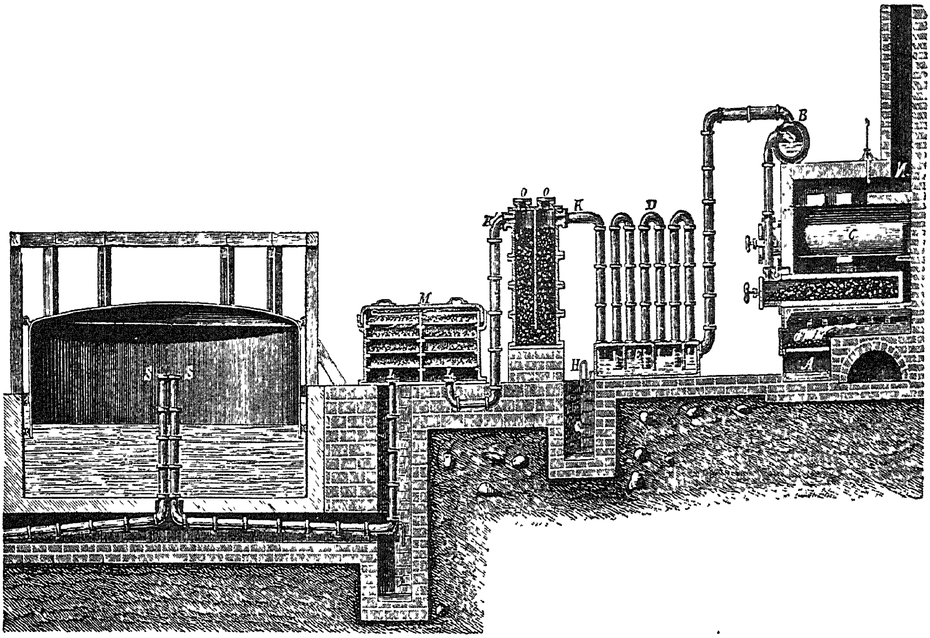


Fig. 65.

C = horizontal retorts; *B* = hydraulic main for separating the tar; *D* = tubes for cooling gas, *O* = washing towers (*scrubbers*), *M* = chambers containing Laming mixture for purifying; *G* = single-lift gasholder; *SS* = entry and exit gaspipes.

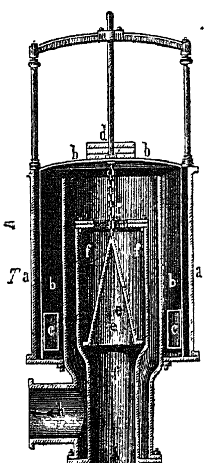


Fig. 66.

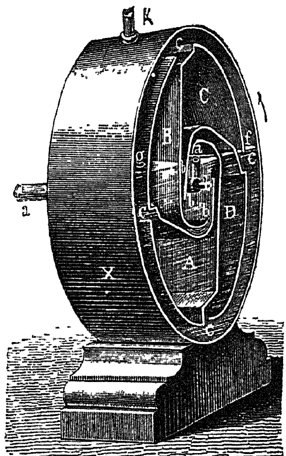


Fig. 67.

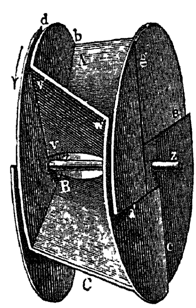


Fig. 68.

The last few years have seen the successful introduction of the new *dry meters* and of *automatic meters*, of which alone Berlin contained 84,000 in 1905. By placing a 10-pfennig piece into one of these automatic meters, 500 litres of gas are supplied. In 1906 Berlin had in addition 191,000 ordinary meters.

YIELD, VALUE, AND PRICE OF GAS. These vary with the nature of the coal used and with the conditions of carbonisation. In the large gasworks of the principal European

towns the yields usually vary between the following limits: coke, 63–76 per cent., more commonly 69–71 per cent.; tar, 4–6 per cent.; ammonia liquors, 9·8–12·5 per cent.; gas, 25–31 cu. metres (of sp. gr. 0·360–0·480). At Berlin every ton of coal yielded on the average 287 3 cu. metres in 1900, 305 in 1901, 320 in 1902, and 324·4 in 1904, in addition to 690 kilos of coke, 54 kilos of tar, and 120 kilos of ammonia liquors.

In many gasworks at the present day, instead of installing new plant, increased consumption of gas is met by mixing with *water-gas* (or *blue gas*), and as the calorific value of this is only about one-half that of coal-gas, benzene or heavy petroleum vapours are also added. Water-gas generators give a rapid production, do not form naphthalene or tar, and yield a gas costing less than half that of ordinary gas; this is, however, very rich in carbon monoxide, which has caused numerous cases of poisoning in the United States, so that the medical men are now (1910) instituting a campaign to forbid the use of water-gas.[1]

The cost of manufacture of bituminous coal-gas varies with the different factors affecting its production, especially with the size of the works, the prices of coal and labour and the greater or less completeness with which the secondary products (ammonia,

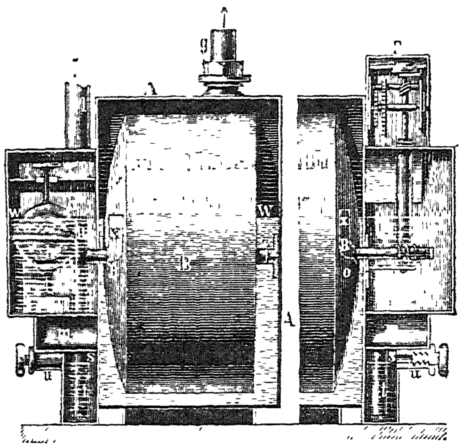


FIG. 69.

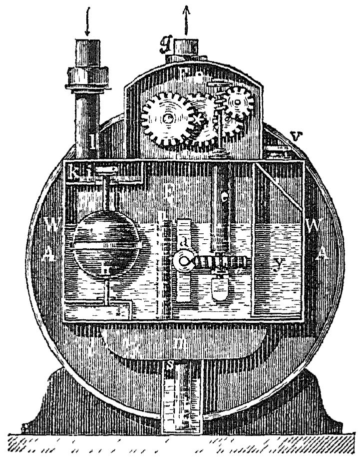


FIG. 70.

cyanides, sulphur, tar, &c.) are utilised. In Berlin the mean cost of manufacture seems to be less than 0·75*d.* per cubic metre, while at Milan it is about 0·85*d.*[2] Gas varies in price in different towns from 1·15 to 3·8*d.* per cubic metre (32-100*d.* per 1000 cu. ft.); in Paris it is 1·9, in Milan 1·25, in Oneglia 2·9, in Messina 3·2, in Venice 3·5, in Catania 3·8, and in Naples 3·1*d.* per cubic metre. [In England often much cheaper.—*Translator.*]

STATISTICS. The consumption of lighting gas (subject to tax) in Italy in 1902 was 139 million cu. metres, and exempt from taxation (for engines, &c.) 56 million cu. metres. In 1898 the total production was 198 million cu. metres; in 1902, 211 million cu. metres; in 1908, 308 million cu. metres obtained from 1 million tons of coal, with a yield of 51,000

[1] Water-gas, reinforced with benzene and mineral oils, costs about 15 per cent. more than ordinary gas but presents various advantages: without expensive plant, a production higher than the capacity of the works can be supplied; part of the coke is utilised, over-production and consequent lowering of the price being thus avoided; less consumption of coal for gas and hence less danger of rise in price of coal; less labour; rapid production even in the event of a strike. In England over 500,000,000 cu. metres are produced per annum. 4 grms. of benzene per cubic metre of gas increase the luminosity by one candle. A mixture of two-thirds of illuminating gas and one-third of water-gas gives a luminosity of sixteen candles when treated with about 40 grms. of benzene, the cost of the latter being about 0·6*d.* per cubic metre.

[2] We give here an approximate industrial balance-sheet referred to one ton of coal and to the conditions employed in the Milan gasworks:

(*a*) *Receipts* · 264 cu. metres of gas (290 actually produced, less 9 per cent for escapes and consumption in works) at 0 13 lira gives 34·32 lire; 700 kilos of coke, 22·40 lire; 45 kilos of tar, 1·35 lira; 9 kilos of ammonium sulphate, 2 70 lire; cyanides, graphite, slag, ashes, 0 06 lira. *Total receipts*, 60·83 lire.

(*b*) *Expenditure:* 1 ton of coal, 30 lire; coke for heating the furnaces (160 kilos), 5 12 lire; purifying and Laming mixtures, 0 37 lira; sulphuric acid and expenses for ammonium sulphate, 1·44 lira; salaries and wages, 10 58 lire; taxes, 0·67 lira; fire insurance, 0 091 lira; workmen's insurance, 0 175 lira; general expenses, 1 10 lira; maintenance of works, private and public expenses, new plant, 3 lire; maintenance of meters and sundry other expenses, 0 090 lira *Total expenditure*, 53 23 lire.

Net profit, about 7·60 lire.

tons of tar and 709,000 tons of coke; in 1909 the gas produced in Italy in 198 works amounted to 318 million cu. metres having a value of two millions sterling. At Milan in 1903, 40 million cu. metres of gas were produced, in 1905 about 47 million cu. metres, in 1907 almost 58 million cu. metres, and in 1908 about 61 million cu. metres (7000 incandescent gas lamps being used for public lighting). Paris alone consumes annually 350 million cu. metres, two-thirds by night and one-third by day (for engines, &c.), and Berlin in 1908 about 250 million cu. metres (in this city gas manufacture is municipalised, and the community draws an annual profit of about £350,000). From 1886 to 1904, the consumption in Brussels increased from 15 to 39 million cu. metres, that is, from 85 to 204 cu. metres per head per annum.

The various sources of light used to supply the needs of Paris in 1889 were in the following proportions: wax, tallow, stearin, 1·6 per cent.; vegetable oils, 4·5 per cent.; petroleum, 17·7 per cent.; electricity, 18·9 per cent.; gas, 57·3 per cent. In Berlin, where the consumption of gas in 1889 was 117 million cu. metres and where 54,000 tons of petroleum were used for lighting purposes, the proportions were as follows: petroleum, 50 per cent.; gas, 47 per cent.; electricity, 3 per cent.

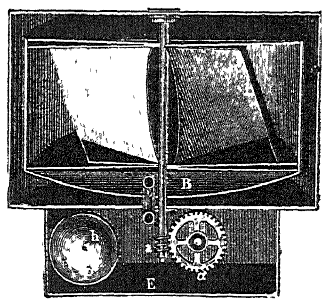


FIG. 71.

England carbonises annually 16 million tons of coal (in 1906) to procure 4500 million cu. metres of illuminating gas. Germany, in 1896, distilled 2,727,000 tons and consumed also one million tons of petroleum, equivalent to 2000 million cu. metres of gas; in 1905, 310 large gasworks used 4,500,000 tons of coal, of which one-fourth was imported from England, and 700 other small works carbonised a total of 1,000,000 tons; in 1910, the total coal used for gas in Germany amounted to about 6,500,000 tons,[1] one-half the total production being used for gas-engines, of which there were 35,000 developing 170,000 horse-power (in 1898 there were about 22,000 gas-engines using 33 per cent. of the total gas produced).

In the United States 1640 million cu. metres of lighting gas were produced in 1907, the value being £3,200,000. In 1909 the United States contained 1296 gasworks with a capital of £183,107,400, the number of officials being 13,515 and the number of operatives 37,215. The output of gas and other products was valued at £33,400,000, and 53 per cent. of the total production consisted of water-gas. In Japan the industry was started only in 1901, and in 1907 the production had reached 44 million cu. metres.

The manufacture and nature of air gas, producer gas, suction gas, Riché gas, water gas, &c., are described in vol. i (p. 393).

PHYSICAL AND CHEMICAL TESTING OF ILLUMINATING GAS. As regards the determination of CO, CO_2, N, and O, Orsat's apparatus (*see* vol. i, p. 375) gives good results. The estimation of hydrogen is effected with the ordinary Hempel burette or simply by determining the diminution in volume of the gas after passing it through a capillary tube containing palladinised asbestos heated at about 100° (*see* vol. i, p. 137). Then comes the determination of unsaturated and aromatic hydrocarbons, which are all absorbed by fuming concentrated sulphuric acid, the gas being measured before and after the absorption in the Hempel burette (the gas being washed with potash after the absorption). The methane is estimated by exploding the gas remaining in the burette with a known volume (in excess) of oxygen by means of an electric spark, 2 vols. of the gaseous mixture (gas + oxygen) disappearing for every 1 vol. of methane, according to the equation:

$$\underset{\text{1 vol.}}{CH_4} + \underset{\text{2 vols.}}{2O_2} = \underset{\text{1 vol.}}{CO_2} + \underset{\text{condenses}}{2H_2O}.$$

[1] For the production of gas in Berlin 352,000 tons of German coal and 397,000 tons of English coal were used; at the English ports the coal cost 8*s.* 1½*d.* per ton in 1904 and 11*s.* 4½*d.* in 1909. The cost of transport from the English mines to Berlin amounted to 7*s.* 3½*d.* per ton, whilst from the German mines at Ruhr to Berlin it exceeded 8*s.* 11*d.* At the gasworks in Berlin the English coal cost 16*s.* 3*d.* per ton, and the German (from Silesia) 20*s.* 4*d.* per ton. In Germany 44 million cu. metres of gas were consumed in 1859, 350 million cu. metres in 1879, about 500 million cu. metres in 1889, almost 1200 million cu. metres in 1899, and about 1800 million cu. metres in 1908, there being 1200 factories, representing a capital of £80,000,000 (for Berlin alone £12,000,000 and for Munich £640,000). In 1880 only one-half of the gasworks were municipalised, and in 1909 two-thirds, the profit amounting to 8 to 13 per cent. on the capital.

To estimate the *ammonia* in the purified gas, 200 litres of it are passed through 10 c.c. of an N/10 solution of hydrochloric acid, the excess of which is subsequently determined by titration.

The determination of the total *sulphur compounds* can be simply effected, according to F. Fischer, as follows: About 50 litres of the gas (measured by a good meter) are burned in a small Bunsen burner, *g* (Fig. 72), in the drawn-out bulb, *A*, of a bulb-condenser arranged as shown. All the sulphur of the sulphur compounds burns, forming sulphurous and sulphuric acids with the water from the combustion of the gas, this condensing in the bulbs of the condenser and being collected at the bottom in a beaker by means of the tube *e*. The combustion is regulated so that gas containing 4–6 per cent. of oxygen escapes at *o*. Water enters the condenser at *z* and leaves at *n*. At the end of the operation, the bulbs are rinsed out with water and the sulphurous acid in the liquid oxidised by means of pure, neutral hydrogen peroxide solution; the sulphuric acid is then titrated with N/10 sodium hydroxide solution. If the sulphuric acid is estimated gravimetrically with barium chloride, the oxidation of the sulphurous acid must be effected with hydrogen peroxide free from sulphates. The quantity of sulphuric acid found gives the total sulphur-content of the gas. A well-purified gas contains less than 0·5 grm. of sulphur per cubic metre.

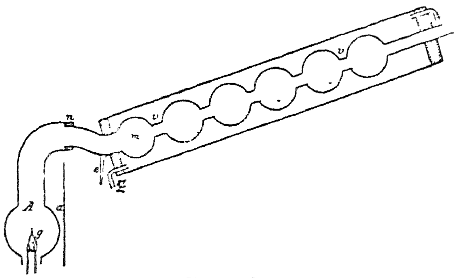


FIG. 72.

The *hydrogen sulphide* is estimated separately by passing a known volume of the gas through ammoniacal silver nitrate solution, which is afterwards acidified with a little nitric acid, the silver sulphide being filtered off, washed, dried at 100°, and weighed.

The *calorific power* can be determined fairly rapidly by means of the Junker *calorimeter* (Fig. 73, section, and Fig. 74), which consists of a metal cylinder, *C* (the letters refer in all cases to Fig. 74), which is mounted on three feet, and inside which a known volume of the gas is burned by means of the Bunsen burner, *n*. The hot products of combustion pass several times up and down the calorimeter and issue at the outlet *S*, which is furnished with a valve and also regulates the air-draught. Passing in a direction opposite to that of the gases of combustion and in alternate adjacent chambers is a current of water which enters by *w* the small reservoir *m*, the excess being carried off by the overflow, *b*, while a regular stream passes through the tap *e* (furnished with an indicator) into the calorimeter at a temperature given by the thermometer *x*, and flows away at *c* at a higher temperature, shown by the thermometer *y*. When the combustion is started, the entry of water is regulated by means of *e*, so that the thermometers, *x* and *y*, indicate a temperature difference of 10–20°; when the flow of both gas and water is constant, the thermometer *y* soon shows a constant temperature.

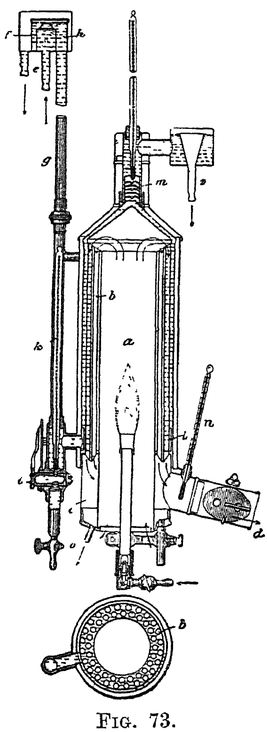


FIG. 73.

The gas is measured by the meter, *G*, and then passes through the regulator, *P*, to the Bunsen burner, *n*, which is drawn from the calorimeter to be lighted and is then pushed in again to the height *q* (about 6 in. up). If the apparatus is in order, no water should fall from *d* into the cylinder, *v*.

When water is discharging from *b* and from *c*, and the thermometer remains stationary, as soon as the index of the meter reaches the zero mark or a definite number of litres, the rubber tube *c* is instantly placed from *t* into *V*, which is a graduated cylinder placed quite close to the discharge-funnel, *t*. In the cylinder *V* is collected all the water which is discharged during the combustion of a definite volume of gas (in the proportion of

100 to 200 litres of illuminating gas or 400 to 800 litres of suction gas or Dowson gas per hour). Exactly at the moment when the meter indicates the volume of gas fixed upon, the rubber tube, *c*, is removed from *V* to *t*. During the course of the experiment the small variations in the indications of the thermometer *y* are noted at intervals, the mean temperature being subsequently determined.

The graduated cylinder, *v*, contains the condensed water (*a* c.c.) formed during the combustion of the gas, and this, in condensing, has given up to the water of the calorimeter a certain quantity of heat, which must be subtracted before calculating the *net calorific power*. The *gross calorific power*, *U*, expressed in calories per cubic metre, is calculated by means of the formula: $U = \frac{A\ T.1000}{Q}$, where *A* indicates the quantity of water in litres collected in *V*, and *Q* the volume of gas burned. If, for example, $Q = 3$ litres, $A = 0{\cdot}900$, $T = 18°$ (that is, 26·77°, the mean of six readings of the thermometer *y*, less 8·77° shown by the thermometer *x* to be the temperature of the water entering at *e*), we have $U = \frac{0{\cdot}900.18.1000}{3} = 5400$ Calories per cubic metre of gas. In cases where the gas is used in engines or other apparatus from which the products of combustion issue at a temperature above 65°, the water-vapour does not condense and the *gross calorific power* must be diminished by the heat due to the condensation of the water-vapour produced by the combustion of the gas in the calorimeter. From *U* must hence be subtracted a value obtained by multiplying by 60 the number of c.c. of water condensing during the combustion of 10 litres of gas. This *net calorific power*, U^1, is, for illuminating gas, usually 10 per cent. lower than the *gross calorific power*, *U*.

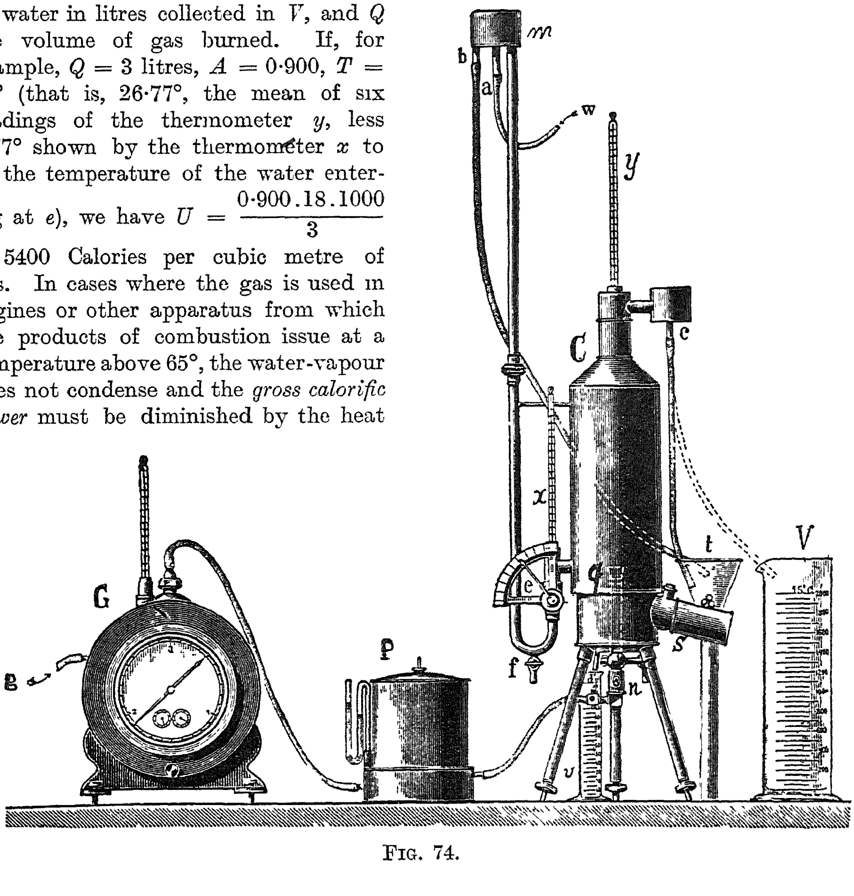


FIG. 74.

The *specific gravity* sometimes serves to test the constancy in composition of gas or to compare two different gases; it also gives a rough idea of illuminating power, since the specific gravities of the more highly light-giving hydrocarbons—acetylene (0·920), ethylene (0·976), propylene (1·490), and benzene (2·780)—are higher than those of the non-luminous components—hydrogen (0·0695), methane (0·559), &c. The specific gravity can be determined rapidly and exactly with the Bunsen *effusiometer* (*see* vol. i, p. 39).

ILLUMINATING POWER. There is no absolute measure of the power of different sources of light, but these can be compared when a conventional unit has been chosen.

This *standard of light* has been differently chosen in different countries and has been

continually modified. Thus in England spermaceti candles are used of such size that six weigh 1 lb., while, when burned, they lose 7·78 grms. (120 grains) per hour with a flame 45 mm. in height. In Germany in 1872 a paraffin candle 20 mm. in diameter was employed, the wick having 24 threads and weighing 0 668 grm. per metre and the flame being 50 mm. high; six of these candles weighed 1 lb. Use is now made in Germany of the more rational Hefner-Alteneck lamp, fed with a liquid of constant composition, namely, amyl acetate, the compact wick, 8 mm. in diameter, protruding 25 mm.

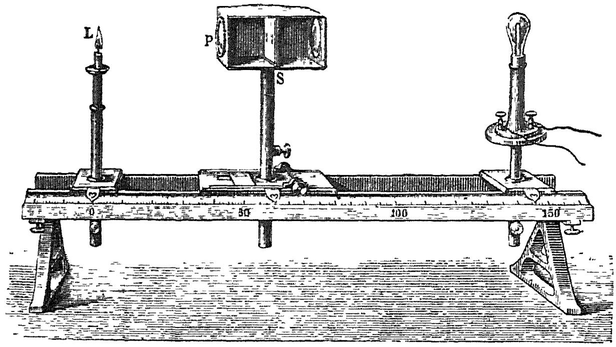


FIG. 75.

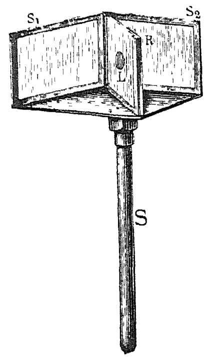


FIG. 76.

from the metallic sheath holding it; the flame is 40 mm. high. In France and Italy the Carcel lamp is used, this consuming 42 grms. of purified colza oil per hour and having a wick which is 23·5 mm. in diameter, is formed of 75 threads, and weighs 3·6 grms. per 10 cm.

The relative values of these different units is as follows: 1 Carcel = 9·600 English candles (spermaceti) = 8·768 German candles (paraffin) = 10·526 Hefner-Alteneck flames.

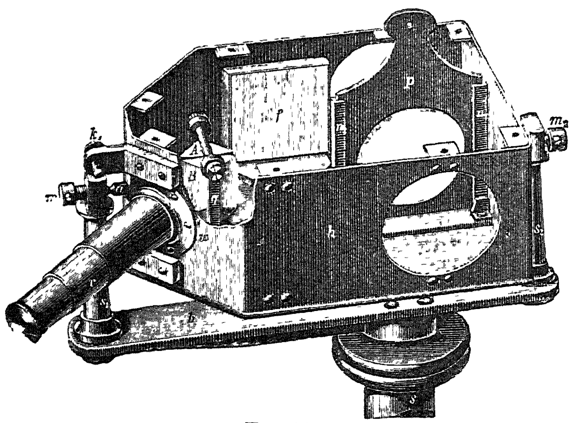


FIG. 77.

The luminous unit being fixed, different sources of light and their illuminating powers can be compared by means of *photometers*. Of these, the one most largely used is that of Bunsen, which is based on the principle that the intensity of light produced on a definite surface by a source of light is inversely proportional to the square of the distance. If the distance between the source of light and the surface illuminated is trebled, the intensity of the illumination is diminished to one-ninth of its previous value. The luminosities of two flames, I and I_1, which illuminate equally a given screen and are at the respective distances, L and L_1, from it, are directly proportional to the squares of these distances: $I : I_1 = L^2 : L_1{}^2$, and if I_1 is the unit of measurement, the intensity of the other source of light will be: $I = \frac{L^2}{L_1{}^2}$. The Bunsen photometer (Fig. 75) consists of a horizontal iron photometer bench 3 metres long and divided decimally (into half-centimetres or millimetres); at one end is placed the comparison electric or candle lamp or the Carcel lamp, the consumption of oil in which is regulated by a small pump actuated by a clockwork mechanism, weighing on a balance the consumption in a given time (indicated by a bell)—this corresponding with 42 grms. of oil per hour. A screen of paper can be moved backwards and forwards along the bench and normally to it, the middle of the screen being rendered translucent by means of a grease spot (spermaceti); at the other end

of the bench is placed the light to be examined. When the screen is equally illuminated on its two faces, the grease-spot is no longer perceptible. The intensities of the two sources of light are then proportional to the squares of their distances from the screen.

The measurement is made in a dark room and, in order to render more evident the disappearance of the spot on the two surfaces, the screen is placed between two mirrors arranged at an angle (Fig. 76). An improvement on the Bunsen photometer has been made by Lummer and Brodhun, who substitute for the screen with the grease-spot a closed box, *h* (Fig. 77), in which are two opposite circular apertures, these illuminating the two faces of a white screen, *f*, by means of light from the standard lamp, and that to be tested placed at the two extreme ends of the photometer bench. By means of a system of prisms, *A B*, the two faces of the white screen reflect the light on to two concentric zones of the field of the eye-piece, *r*. When the two faces of the screen are equally illuminated, the two zones of the field also appear uniformly lighted.[1]

OIL-GAS

In cases where the installation of a plant for the carbonisation of coal would be inexpedient, owing to the small consumption of illuminating gas, it may be convenient to prepare oil-gas by dropping into a red-hot retort (*see later*, "Cracking" Process in the Petroleum Industry) fatty residues, tar oils, resins, and petroleum. This destruction by heat produces a gas which can be readily compressed without separation of liquid, and, enriched with 25 per cent. of acetylene, is used for the illumination of railway carriages. Oil-gas can also be prepared easily and abundantly by dropping oil into gasogens containing red-hot coke.

As early as 1815 public lighting with oil-gas was attempted (Liverpool used it for some years), but it was only after 1860–1870 that this industry assumed importance. From 100 kilos of lignite paraffin oil are obtained 60 cu. metres of gas, and with a consumption of 35 litres of the gas per hour, 7·5 normal candles (German) are obtained; its illuminating power is four times as great as that of ordinary lighting gas. If a greater yield of the gas is obtained, it loses in illuminating power. The purification of oil-gas is carried out in practically the same way as that of coal-gas. Mineral oil for gas and for engines is produced in large quantities in Galicia, where it is sold for less than 19·5*d*. per cwt. (4 lire per quintal); Germany alone imported 30,000 tons of it in 1909.

[1] **Comparison between Various Sources of Light** To produce the luminous intensity of a Hefner candle-hour (HK), the following quantities of lighting materials must be consumed:

Candles	Stearine, first quality	7·87	grms.
	,, third ,,	9·58	,,
	Paraffin	6·27	,,
	Two parts of paraffin and one of stearine	6·93	,,
Lamps	Carcel: colza oil	3·99	,,
	Petroleum, flat wick	2·76	,,
	,, round wick	2·80 / 3·60	,,
	Spirit: incandescent	1·90	,,
	Petroleum with Auer mantle	0·50	,,

	Acetylene	0·6	litres
Gas burners	Fish-tail	19·0	,,
	Argand	10	,,
	Auer	1·60	,,
	Millenium (gas under pressure)	0·75	,,
	Auer with inverted flame	0·70	,,
Electric lamps	Arc lamp of small power	1·20	volt-amps
	Arc lamp of high power	0·25	,,
	Incandescent Edison	3·70	,,
	Metallic filament (osmium, tantalum)	1·90	,,
	Mercury vapour	0·50	,,

It is easy to calculate the cost from the prices of the various methods of lighting, these varying from town to town and from country to country. In 1896 Lüpke calculated the following numbers of normal candle-hours to be obtainable for one mark (one shilling), the calculation being only valid for that period and for Germany: wax, 33; stearine, 77; colza oil, 150; electric lamp with incandescent carbon filament, 150; fish-tail gas-jet, 625; acetylene and air with an edged burner, 716; oil-gas, 1660; water-gas with benzene, 1666; electric arc lamp, 2232; Auer gas lamp, 2300; Auer water-gas lamp, 4350.

From gas at 1·9*d* (0·2 lira) per cubic metre, as a source of heat, 1000 cals. are obtained for 0·38*d*. (0·04 lira), whilst, using electric current at 3·07*d*. (0·32 lira) per kilowatt-hour, 1000 cals. would cost about 3·65*d*. (0·38 lira). For power purposes, the electric current [at 2·4*d*. (0·25 lira) per kilowatt-hour] costs more than double as much as gas [at 1·73*d*. (0·18 lira) per cubic metre].

During the past few years a considerable advance has been made by the use of incandescent electric lamps with metallic filaments (tantalum, tungsten, osmium, &c.), which reduce the consumption of electrical energy by one-half. But at the same time gas lamps have been improved by the use of high-pressure gas, and those with inverted flames are still decidedly more economical than metallic filament electric lamps. From the hygienic point of view the disadvantages of gas lighting have been exaggerated, as it has not been realised that the use of gas causes circulation and renewal of the air, and that the production of water-vapour and carbon dioxide are negligible compared with the similar effects produced by the respiration of human beings.

PETROLEUM INDUSTRY

Crude petroleum also goes under the name of *mineral oil* or *naphtha*, and is a more or less dark liquid (according to its origin) with a peculiar, pronounced odour. It is found in various parts of the earth in the strata of the tertiary epoch and also of preceding epochs. The principal centres of production are Baku (Russia) and the United States.[1]

In some places it overflows at the surface of the earth through porous rocks or clefts; in others it is found accumulated under pressure in large cavities or pockets, since when it is reached by borings or wells, powerful jets rise above the surface of the earth often to the height of 100 metres, thus forming fountains of petroleum which last from a few weeks up to seven or eight months and throw up also large quantities of inflammable gases and sand.

Some petroleum deposits have been gradually evaporated and oxidised

[1] **History of the Petroleum Industry.** The use of petroleum and of tar goes back to the earliest historical times (the Biblical legend relates that Noah rendered his ark impermeable by means of tar, and in the construction of the Tower of Babel a mortar was used prepared with naphtha ! (?)) Certain races then employed naphtha as a combustible, and the Egyptians made use of it in the preparation of mummies.

In small quantities petroleum is found in nearly all countries, but 95 per cent. of the total production is given by North America and Russia. Two centuries before petroleum was used in America that from Parma in the Apennines was used for lighting, *e g.* at Genoa, Parma, &c. The most important petroleum wells now in Italy are in the Province of Piacenza (at Fiorenzuola d'Arda) and at Salsomaggiore, Borgo S Donnino, and Montechino; less important deposits are found also in Calabria. At Velleia the industry has been worked for many years by a French company, many wells 200 to 450 metres deep having been sunk along the right bank of the Chero; this company was absorbed by an Italian syndicate in 1907.

In Austria the region richest in petroleum is Galicia In 1895, when a well 300 metres deep was bored, a fountain was formed which, in thirty-six hours, yielded 5000 barrels of petroleum (1 barrel = 42 gallons = 159 litres = 145 kilos). Still more important wells in other countries are mentioned on p 66.

In Russia the most important sources of petroleum are found in the province of Baku (99 per cent of the whole production is obtained from an area of 6 sq. kiloms), and partly at Grosny, to the north. From the most remote times, before Christ, *sacred fires*, fed by petroleum and by the inflammable gases liberated from it, have been kept burning uninterruptedly in the temples (down to 1880) During his voyage in the thirteenth century Marco Polo visited these marvellous springs of "*oil not good to use with food but good to burn and also used to anoint camels that have the mange.*"

In 1820 the Baku petroleum wells were declared the property of the Russian State, and the Government made concessions to contractors who worked them in a primitive manner until 1872. In 1873, the most important wells and petroleum-bearing lands were put up for auction by the Government, who levied a tax on the petroleum extracted. This condition of affairs was less favourable than that holding in the American industry, so that in 1877 the tax was repealed and the Russian petroleum industry, passing into the hands of great capitalists (Nobel, Rothschild, &c), underwent extraordinary development and often competes advantageously with that of America.

The first plant installed by Baron Thormann for the distillation of petroleum was constructed at Baku in 1858 according to suggestions and plans furnished by Liebig, carried out by one of his assistants (Molderhauer), and improved by Eichler. The first wells bored on the American system date from 1869. Before 1870, the production was only 250,000 poods (1 *pood* = 16·38 kilo), but in 1872 it reached 1,500,000 poods and then grew with astounding rapidity (*see later*, Statistics).

There are also important petroleum deposits in Japan, but the production is still limited: in 1874 it amounted to 126,150 kwan (1 *kwan* = 3 78 kilos), in 1884 to 1,400,000 kwan, and in 1903 to about 126,000 tons.

During recent times important sources of petroleum have also been discovered in Canada.

The greatest impulse to the petroleum industry has come from the United States of America, where important deposits of petroleum have been found, first in the State of Pennsylvania (in a strip of land about 100 kiloms. long, the production of petroleum increased from 3180 hectolitres in 1859 to 16,000,000 hectolitres in 1874, the price per barrel falling during the same period from 100 lire or £4 to 6·5 lire or 5*s* $2\frac{1}{2}d$; these deposits are now apparently becoming exhausted), and then in Virginia, Ohio, Indiana, California, Louisiana, and Texas. At the present time the most important sources of petroleum in the United States are in the Washington district.

The first studies on petroleum in America were made by Silliman in 1854, by fractional distillation, and these were followed by unsuccessful industrial efforts caused by the low production of the wells utilised and by many commercial difficulties, which were overcome by L. Drake in 1859 by the use of artesian wells.

The first petroleum well in America was obtained by pure chance; at Titusville in Pennsylvania a well was being sunk for drinking water and when a depth of 22 metres was reached, a continuous jet of petroleum appeared yielding 4000 litres of naphtha per day

Just as America was taken with the "gold-fever" after the discovery of gold in California, so the United States caught the petroleum fever. Pennsylvania was invaded by adventurers, and borings were made wherever the geological formation of the earth admitted of it, all had faith in the goddess Fortune, who, as always, favoured some and drove others to ruin and despair. In 1861 the number of *derricks* (used for boring) exceeded 2000. The work was carried out hastily and without thought, usually empirically, the idea being to succeed first. Much petroleum was lost, and much was burnt, causing immense losses and ruin to numerous firms.

Great capitalist companies were then formed and these studied calmly and rationally the technical and commercial problem and very soon created an enormous industry, which rapidly brought petroleum into common use all over the world. Ships and railways and then iron pipes ten and hundreds of kilometres in length served to transport the petroleum rapidly, continuously, and economically from the wells to the refineries and from these to the seaports, where it was shipped to the merchants.

during the lapse of ages, leaving a black deposit of *mineral tar* or *asphalte* (*see* section on Paraffin).

ORIGIN OF PETROLEUM. Various hypotheses have been put forward to explain the origin of petroleum, and even to-day opinions are divided, probably owing to the fact that petroleum has not one single origin, since, in different parts of the earth's crust, it has different qualities and compositions.

(1) *Hypothesis of Inorganic Origin.* A. v. Humboldt supposed petroleum to have originated from inorganic gaseous products under the influence of volcanic forces, and in 1866 Berthelot advanced the hypothesis that, by the action of carbon dioxide on alkali metals inside the earth's crust, acetylides would be formed which with hydrogen would give acetylene derivatives, these then undergoing various condensations to form petroleum and tar. Byasson in 1871 explained the formation of the hydrocarbons of petroleum as due to the action of H_2S, CO_2, and water-vapour on layers of red-hot iron, this action being produced by the infiltration of sea-water, through clefts at the bottom of the ocean, in such a way that, together with calcareous matter, it was brought into contact with deposits of heated iron or iron sulphide. Mendelejeff (1877) regarded the hydrocarbons of petroleum as originating in the igneous strata of the earth's crust by the action of aqueous infiltrations on pre-existing deposits of carbide of iron or other metallic carbides. From 1877 to 1879 Cloëz obtained support for Mendelejeff's hypothesis by showing experimentally that saturated hydrocarbons are formed when cast iron or spiegeleisen (substances which contain carbide of iron) is dissolved in acid. In 1891 Ross brought forward again and modified Byasson's hypothesis; he assumed that volcanic gases, especially H_2S and SO_2, in contact with heated chalky rocks, would form gypsum, with separation of sulphur and production of saturated and unsaturated hydrocarbons (this would also give an explanation of the origin of sulphur, yet in Sicily, where sulphur abounds, no petroleum is found !).

These various hypotheses on the inorganic origin of petroleum assume the formation of the latter in igneous primitive (archaic) geological strata, where the presence of organic compounds is excluded, the petroleum then finding its way to the higher layers of the earth's crust by seismic convulsions. But it is precisely these older archaic strata, deprived of water and of organic substances, which give no trace of petroleum. On the other hand, if the petroleum were formed in very hot strata, it should issue from the borings at a moderately high temperature, and there should have been separation of the light petroleum (more volatile) and the heavy into distinct layers. But this is not actually the case.

However, during recent years this hypothesis has again come into favour, owing to the interesting work of Moissan (1894–1896) on the formation of saturated hydrocarbons by the action of water on aluminium carbide (*see* p. 34), and that of Sabatier and Senderens (1896–1902), who showed experimentally that, in presence of catalytic nickel (obtained by reduction of the oxide with hydrogen at 300°), hydrogen and unsaturated hydrocarbons (ethylene, acetylene, &c.) give rise to saturated hydrocarbons such as occur in petroleum (p. 34). But even these syntheses do not yield very high and solid hydrocarbons like those present in crude petroleum, although recently (1908–1909) A. Brun, Stieger, and Becker showed that hydrocarbons similar to paraffin are formed by the interaction in the hot of iron carbide and ammonium chloride, even in absence of water.

(2) *Hypothesis of the Vegetable Origin of Petroleum.* This was enunciated at intervals by Binney (by distillation of peat), by Kobell (by distillation of coal), and by Bischof, who considered petroleum to be formed by the action of sea-water on cellulose and on coal included in the geological strata of the earth's crust. This hypothesis of the vegetable origin was later supported or attacked by various writers, and to the fact that, in general, carboniferous strata do not contain petroleum, is opposed the discovery of small deposits of petroleum in the coal-seams near Wombridge and of certain petroliferous substances in Japanese coals; but Höfer showed that, in the first case, the neighbourhood of bituminous schists, rich in the remains of fishes, could not be excluded, and, if it is desired to explain the formation of petroleum from marine vegetable organisms, it is not possible to conceive of a sufficient quantity of these to give rise to the immense amounts of petroleum now discovered. Further, other more recent geological investigations would exclude the vegetable origin of petroleum, although the most recent chemical work tends to render such origin highly probable. It is, indeed,

found that petroleum rotates the plane of polarisation of light to the right (*see later*), as do most optically active vegetable substances, whilst substances of animal origin rotate it preferably to the left. Engler, however, states that this observation is not very conclusive, since these active substances may be due to the condensation of unsaturated products originating in the decomposition of the prime materials (animals or possibly vegetables). Krämer and Potonié (1906–1907) point out that all petroleums (also certain lignites and ozokerite) contain *algæ wax*, from which, by various reactions and decompositions, it is easy to pass to substances like petroleum, and simple substances, by polymerisation (by heat and pressure), form more complex tarry substances, &c. ; the presence of wax demonstrates that petroleum is not formed in the hot by distillation, but rather in the cold and at high pressures. The prime material of petroleum would hence probably be the enormous formation of *algæ* which have been produced at all epochs and are to-day accumulating in marshy places. These, during thousands of centuries and under the action of pressure and heat, could undergo the same transformations and putrefactions (mixed sometimes with animal remains), leaving the wax for the formation of petroleum ; so that petroleum would be formed in all epochs and is perhaps being formed now ! The varying composition of petroleum would be due, according to Krämer, to filtration through various geological strata, which would have removed greater or less quantities of bituminous products so as to produce pale, light petroleums like those of Velleia and Montechino. Hence the greater or less content of tarry substances cannot serve as an indication of the epoch of formation of a petroleum, since part of these substances may have been lost during the geological filtrations.

(3) *Hypothesis of the Animal Origin of Petroleum.* This was enunciated and vigorously upheld by Hofer, and supported and supplemented by Ochsenius (1892), Zaloziecki (1892) Veith, Dieckhoff (1893), Aisinmann (1894), Heusler (1896), Holde (1897), Aschan (1902), and Zuber (1897, who supported only the organic origin), and more especially and most exhaustively by Engler (1888–1901).

This hypothesis supposes that great layers of various fishes and molluscs, formed on the ocean-bed during past geological epochs, gradually underwent decomposition, first losing the nitrogenous components (albuminoids) as gaseous or soluble compounds, the remaining fats being slowly transformed partially into bituminous substances. These, together with the residual fats, under the action of great pressure and heat (developed, in part, by these decompositions) would yield glycerol, which would generate acrolein and then aromatic hydrocarbons, while the remaining fatty acids (by the action of hydrogen formed in all these decompositions) would give rise to the various saturated hydrocarbons constituting petroleum, CO_2 being liberated.

The animal origin hypothesis is also supported by the observation made by Fraas, that petroleum issues from the coralliferous banks of the Red Sea, and by the odour of petroleum exhibited by certain phosphorites which are undoubtedly of animal origin.

The objection has been raised that, if petroleum were of animal origin, it should contain nitrogenous compounds. Although this is not necessary, yet the presence of nitrogen products (ammonia and pyridine bases, free nitrogen and ammonium carbonate) has been shown in petroleum and in gases emanating from the earth. Texas petroleum contains up to 1 per cent. of nitrogen.

Engler showed experimentally that, under certain conditions, animal fats can be transformed into olefines or analogous products in the laboratory (by distilling fish-oil under 4–10 atmos. pressure). In 1909, Engler, Routala, Aschan, and others effected the laboratory production of *naphthenes*, paraffins, and heavy mineral oils, by heating amylene and hexylene under pressure and in presence or absence of aluminium chloride as catalyst.

Many facts support the view that the petroleum of the geological strata studied has been formed at a low temperature and by slow but continuous reactions lasting for thousands of years.

To the doubt that may be raised as to the enormous quantity of animal remains necessary to explain the large amounts of petroleum being raised at the present time, it may be answered that if the annual catch of herrings on the coasts of the northern seas and that of sardines by French fishermen were to accumulate on the ocean-bed for 2000 years, it would be quite sufficient to explain the petroleum production of Russia.[1]

[1] In 1903 the *fish* caught by 103,000 fishermen along the 6000 kiloms. of Italian coast weighed 62,000,000 kilos (15,000,000 in Sicily) and had a value of about £800,000 (in 1904, only £620,000). In the valleys of Comacchio during the month of October 1905, alone, were caught: 450,000 kilos of eels, 60,000 of mullet, 50,000 of various

It would, however, be necessary, for the preservation of this enormous cemetery of fish, that the corpses should not be eaten by other larger fish; the conditions must then be such that fish approaching the cemetery are killed. And this is highly probable, as the existence of such conditions at the bottom of the Black Sea has recently been proved. In fact, below a certain depth, there is so much dissolved hydrogen sulphide that any animal is instantly poisoned there, its body going to swell the vast numbers that have preceded it at the bottom.

With these proofs is connected the most recent and most rational interpretation of the origin of petroleum. It is supposed that the decomposition of the residual animal fats is aided by certain ferments as yet not studied—anærobic bacteria analogous to those which have been studied in the cases of the transformation of wood into coal, the fermentation of cellulose, peat, &c. And the hydrogen sulphide formed at the bottom of the sea would be a product of the fermentations due to these bacteria.

Rakusin (1905 and 1906) made a new contribution to the explanation of the origin of petroleum, by discovering in various petroleums a slight optical activity, undoubtedly due to substances of organic origin (animal or vegetable). Neuberg (1905–1907) has shown that, in the putrefaction of protein substances, pronounced quantities of optically active acids and amino-acids are formed, and by heating under pressure or dry-distilling a mixture of oleic acid with a little valeric acid, a product is obtained which, after purification, has the characters of naphtha as regards the optical rotation, boiling-point, and other properties. All this supports the organic—probably animal—origin of petroleum, and even if the fats do not give an optically active petroleum, the activity would be imparted by the decomposition products of the proteins. The optical activity of petroleum was recognised as far back as 1835 by Biot, who, however, drew no practical or theoretical conclusions from the observation. Rakusin observed that petroleums exhibit the *Tyndall phenomenon* (vol. i, p. 103) to a more or less marked extent, and since petroleums are sometimes inactive and have varying chemical composition, he regards the different hypotheses concerning their origin as justified. Petroleum, as a liquid, must be considered as intermediate to natural inflammable gas and solid asphalte or ozokerite. Since the white *cerasin* which is extracted from *ozokerite* is *dextro-rotatory*, it must be concluded that ozokerite is of organic origin (the products formed by synthesis from simpler or artificial substances being optically inactive, *see* p. 22).

The petroleum or similar substances prepared artificially from the elements possess all the properties of true petroleum, but are optically inactive. Hence the most certain criterion of the organic origin of a petroleum is its optical rotation. If a petroleum is optically inactive, it may have originated from a *racemic* product (optically and transitorily inactive, *see* p. 19) of organic origin, but may have been formed from inorganic materials. However, inactive petroleums are rare; Rakusin (1907) has only found three such up to the present, one Russian (Surakhany) and two Italian (Montechino and Velleia), and he states that not only the degree of carbonisation of the petroleum (richness in carbon), but also its degree of racemisation must be taken account of in judging its geological age.

small fish (acquadelle), whilst in October 1910, 985,000 kilos of eels and mullet were taken. Italy is, however, considerably behindhand in the fishing industry, owing to insufficient study of its seas and to the great technical deficiency of the methods employed by the fishermen, while the speculation of a few merchants makes fish in the great cities of Italy much dearer than in other countries. Consequently, Italy imports continually increasing quantities of fish of all kinds, the value of that imported during 1907 being over £3,000,000. In Germany in 1902, 31,000,000 kilos of herrings worth £400,000 were caught, and in the ports of the Elbe and Weser fish of the additional value of £640,000 was taken In the United States with 134,000 fishermen, fish of the value of £10,000,000 was caught in 1903; and in 1909, 219,500 fishermen took 1,000,000 tons of fish of the value of £12,000,000, including 100,000 tons of oysters worth £3,100,000, and 40,000 tons of cod of the value £480,000. In France 95,500 fishermen caught fish worth about £4,700,000 in 1902, and in Norway 101,000 fishermen took £3,200,000 in 1905. In Holland 21,000 fishermen earned £900,000; in England 106,500 fishermen, £9 000,000; and in Spain, 121,400 fishermen £1,800,000

In the Caspian Sea during the winter of 1906, 129,000 seals were killed, the yield of oil being 2,245,000 kilos, and its value £25,000, without considering the fat and skins, each of which costs 8*s*. to 10*s*. On the coast of Tonquin 30,000,000 kilos of fish were taken in 1893.

To obtain an idea of the fertility of certain fish, the *shad*, a fish of the herring family, weighing up to 5 to 6 kilos, may be considered; the female lays as many as 100,000 eggs, which can be fertilised artificially, as is done with the salmon and trout. In North America the eggs are collected and despatched to the Central Pisciculture Station at Washington, where they are hatched in four days in Macdonald or Weiss tanks with flowing water at 18° to 19°, and are immediately placed in the rivers, where they grow rapidly. Every year more than 100,000,000 eggs are fertilised in this way and from 1875 to 1890 the shad fishing showed an increase of 100 per cent, corresponding with £160,000. The female cod may lay as many as 6,000,000 eggs during its lifetime, and the turbot even 9,000,000 In Italy there are only two schools of fishery, whilst in Germany there are thirty-four, in Franc seventeen, and in Japan one for each maritime province.

In 1908, Zaloziecki and Klarfeld held that the optical activity of petroleum is due to the presence of terpenes or colophony; but Neuberg regards it as due to decomposition products of amino-acids (valeric or isocaproic acid) formed from the proteins. Marcusson (1908) combats these last two hypotheses, and shows that it is more probable that the activity is derived from decomposition products (dextro-rotatory) of lævo-rotatory cholesterols (and hence of animal origin, whilst the vegetable ones are dextro-rotatory and yield lævo-rotatory decomposition products). By distilling olein under pressure, Marcusson (1910) obtained hydrocarbons which had an optical activity equal to that of natural proteins and which he regarded as formed from the original cholesterols. By the action of ozone, Molinari and Fenaroli (1908) showed that the Russian and Roumanian petroleums examined by them contained no *unaltered* cholesterol, but this does not exclude the presence of active decomposition products, which, however, would not contain double linkings. In addition to dextro-rotatory compounds, Java and Borneo petroleums contain lævo-rotatory substances which become dextro-rotatory at 350° (as happens when lævo-rotatory cholesterol is heated); also certain inactive fractions become dextro-rotatory when heated. Rakusin, Molinari, and Fenaroli showed that the optical activity increases in those portions of petroleum that have the highest boiling-point.

COMPOSITION AND PROPERTIES OF CRUDE PETROLEUM.

As obtained from the wells, crude petroleum varies in colour from yellowish to pale brown, or even black, according to its origin; it exhibits a marked greenish fluorescence and a characteristic, garlic-like odour. The dissolved gas soon separates spontaneously, and sometimes, on oxidation in the air, petroleum deposits dark, bituminous substances (paraffin, tar). The lighter petroleums are the paler and have an agreeable, ethereal odour, whilst the heavier ones are darker and have an unpleasant odour.

Certain petroleums have recently been found to be radioactive.

The presence of sulphur in petroleum, even if much less than 1 per cent., injures its odour and colour. The specific gravity of petroleum varies from 0·780 to 0·970. Petroleum obtained from Terra di Lavoro, Italy, has a high specific gravity (0·970) and certain Roumanian and Indian petroleums, rich in paraffins, show values higher even than this, sometimes as much as 1·3.

Montechino petroleum has the sp. gr. 0·740; that of Velleia, 0·780; American, 0·800–0·870; Russian, 0·850–0·900; and Galician, 0·827–0·890.

Different petroleums are composed, as a rough mean, of 13 per cent. of hydrogen and 87 per cent. of carbon, small proportions of oxygen, nitrogen, and sulphur compounds being also present. The hydrocarbons present in petroleum are numbered by the hundred, and they belong to different series, one or other of which preponderates according to the source. Thus, Pennsylvanian petroleums are constituted almost exclusively of hydrocarbons of the saturated series C_nH_{2n+2} (derivatives of methane), which are also found in Galician petroleums, &c.

Some petroleums contain as much as 40 per cent. of hydrocarbons solid at the ordinary temperature (paraffin), and these are left after distillation (*e.g.* Java petroleum); usually, however, much less than this is present, American petroleums having only 2·5–3 per cent., and those of Baku sometimes only 0·25 per cent. Different petroleums can be distinguished by means of the ultra-microscope, the paraffin being dissolved in the colloidal condition.

It is maintained by various chemists that the paraffin is not pre-existent in petroleum, but is formed during its distillation. This is contradicted by the fact that some petroleum pipes show deposits of paraffin, and this can also be separated from cold petroleum by special solvents.

Hydrocarbons of the *unsaturated ethylene* series, C_nH_{2n}, preponderate in the petroleums of Burma and are abundant in those from California; Pennsylvanian petroleum contains about 3 per cent. Different petroleums can hence be distinguished by the quantities of bromine or iodine which they fix,

by the amounts of hydrobromic or hydriodic acid then formed (Park and Worthing, 1910) or by the quantities of ozone they take up (Molinari and Fenaroli, 1908).

Hydrocarbons of the same general formula, C_nH_{2n}, but *saturated* (cyclic compounds, so-called *naphthenes*, or derivatives of *cyclopentane*, $CH_2\left\langle\begin{array}{l}CH_2-CH_2\\ \quad\ \ |\\ CH_2-CH_2\end{array}\right.$, or *cyclohexane*, $CH_2\left\langle\begin{array}{c}CH_2-CH_2\\ CH_2-CH_2\end{array}\right\rangle CH_2$) form 80 per cent. of Baku petroleums and occur abundantly in those of Galicia, together with about 10 per cent. of hydrocarbons of the aromatic series (recently (1910) *hexahydrocumene* has been identified).

In a Russian petroleum and also in a Roumanian one, Molinari and Fenaroli (1908) found hydrocarbons derived from naphthenes with two double linkings and having the general formula C_nH_{2n-14} (for example, $C_{17}H_{20}$).

In certain petroleums small quantities of acetylene derivatives occur.

It is found that petroleums produced in localities relatively near to one another often have different compositions; according to David Day this is due to the fact that the unsaturated hydrocarbons diffuse less easily through sandy or other soils, and this system of natural filtration gives rise to various types of petroleum, with preponderance of saturated hydrocarbons in some and of unsaturated hydrocarbons in others This explanation is more reasonable than that the separation has been effected by distillation.

The products that distil below 180° are almost exclusively saturated and those distilling about 200° mostly unsaturated.

The very small quantities of *oxygenated* substances contained in petroleum (often less than 1 per cent. and rarely 5 per cent.) are composed of phenols and organic acids (*e.g.* in Galician petroleum).

The traces of nitrogenous substances found in various petroleums (*see above*) support the hypothesis of the organic origin of petroleum.

Almost all petroleums contain *sulphur*, which is very difficult to remove and imparts an unpleasant odour and bad colour.

Usually the proportion of sulphur is about 0·10–0·15 per cent., but the petroleum of Terra di Lavoro contains as much as 1·3 per cent., while still more is found (up to 3 per cent.) in those of Texas, Ohio, Indiana, and Virginia, from which it has to be separated (*see later*).

The nature of the sulphur compounds present has not yet been completely defined, but the presence of mercaptans, thio-ethers, thiophene, and its homologues (methyl- and dimethyl-thiophene) has been detected. According to Heusler it is only necessary to heat a little of the petroleum with a granule of aluminium chloride to detect the presence of sulphur, hydrogen sulphide being then developed.

Also by fractional distillation and partly by the specific gravity, the four principal types of petroleum can be distinguished. The products distilling below 150° form the *benzines* (*see later*), then up to 280° are obtained illuminating petroleums or *solar oil* (or *kerosene*), and after 300° remain products used for the extraction of paraffin and vaseline (American) or for the preparation of *mineral lubricating oils* (Russian):

Crude petroleum	Specific gravity	Benzine	Solar oil	Residue
Pennsylvania	0·79–0·82	10–20 %	55–75 %	10–20 %
Ohio	0·80–0·85	10–20 %	30–40 %	35–50 %
Caucasus	0·85–0·90	0 2–5 %	25–30 %	60–65 %
Roumania	0·85	3–10 %	70–80 %	10–15 %
Galicia	0·82–0·90	5–30 %	35–40 %	30–50 %
Piacenza	0·74–0·79	25–40 %	55–65 %	4–8 %
Alsace	0·912	5 %	35–70 %	55–60 %

In some of the islands of the Caspian Sea (Tscheleken) is found a petroleum resembling the American type, with a large proportion of paraffin (5·5 per cent.), and in Columbia (S. America) petroleums like those of Russia (Caucasus) occur.

The *Italian petroleums* vary considerably in composition and those of Emilia and Piacenza are so pale and so rich in benzine and poor in residues that it is supposed that they are the condensed more volatile products of more important deposits not yet discovered. In the distillation of the Velleia petroleums at Fiorenzuola d'Arda the little residue obtained is added to the crude petroleum to be refined and thus becomes distributed in the lighting oil, so that the less remunerative residues are never placed on the market. The absence of optical activity in the petroleums of Montechino and Velleia (*see above*) seems to confirm the view that they are derived from more important deposits, in which optically active products would probably be found.

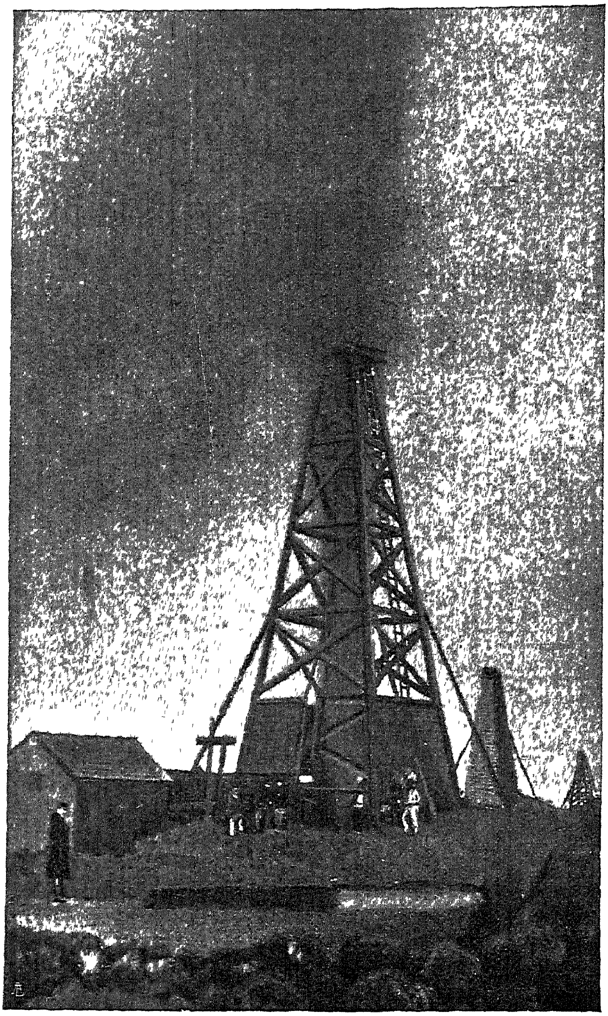


FIG. 78.

EXTRACTION AND INDUSTRIAL TREATMENT OF PETROLEUM. From the most remote times petroleum has been raised in China by means of wells similar to the present artesian ones, which the Chinese used many centuries before Europeans for obtaining drinking water. In other regions in times gone by the petroleum flowing at the surfaces of the water-courses began to be separated and used; then wide, shallow wells were dug and the petroleum raised to the surface in buckets. Nowadays, however, petroleum is everywhere obtained by wells bored into the earth like artesian wells, and sometimes the petroleum flows up to the surface under great pressure, so that it forms a fountain (*see* Note, p. 65, and Fig. 78). It is supposed that the deposits of petroleum in the interior of the earth's crust are situated in large cavities or pockets, where there is often a lower layer of salt water (Fig. 79, *W*) and on this floats a more and less abundant layer of petroleum, *E*; and, in general, the upper part of the pocket is filled with inflammable gas, *G*, which exerts great pressure. If the boring, *B*, reaches one or the other layer, one or the other product is obtained in preponderance or even exclusively, and, after exhausting the aqueous layer, the same well may yield only petroleum.

The sinking of a well is begun with a boring 35–40 cm. in diameter by means of suitable boring tools worked by long rods and toothed gearing, or by compressed-air drills mounted

on wooden structures termed *derricks* (Fig. 80); the detritus of the bored rock is continually carried away from the boring by a current of water, whilst in former times the much slower dry boring was preferably employed. When the petroleum layer is approached, the water of the well or tube begins to show drops of petroleum. The power is often supplied by portable steam-engines, which should not be placed too near the boring, since if the petroleum or gas escapes accidentally in any quantity during the boring, it may ignite and cause considerable damage by fire or explosion.

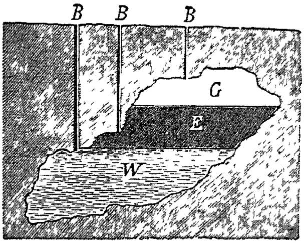


Fig. 79.

In such cases it is hence advisable to transform the energy on the site, for instance, with electric motors. And even then fires and explosions have been caused by the accidental ignition of the gas mixed with air, by sparks formed by stones, issuing violently from the well along with sand and petroleum and striking the iron framework or the rails of the woodwork.[1]

When the petroleum is not exuded under pressure, it is often raised by means of pumps, but this is not possible where much sand (up to 30 per cent.) is also extracted and has to be allowed to deposit; this is the case at Baku, where, however, one-third of the petroleum issues under pressure.

During recent years there have remained relatively few "fountains" at Baku, and the petroleum of the sandy wells, which cannot be raised by pumps, is extracted by special "bailers" made of a cylinder of sheet-metal terminating in a cone and fitted in the lower portion with a valve which opens when the bailer (called a *shalonka*) becomes immersed in the petroleum and closes on raising by means of pulleys and windlass, the steel rope carrying the bailer being wound round a large drum a short distance from the well. The shalonka, containing some hectolitres of petroleum, is discharged by inverting it over a channel.

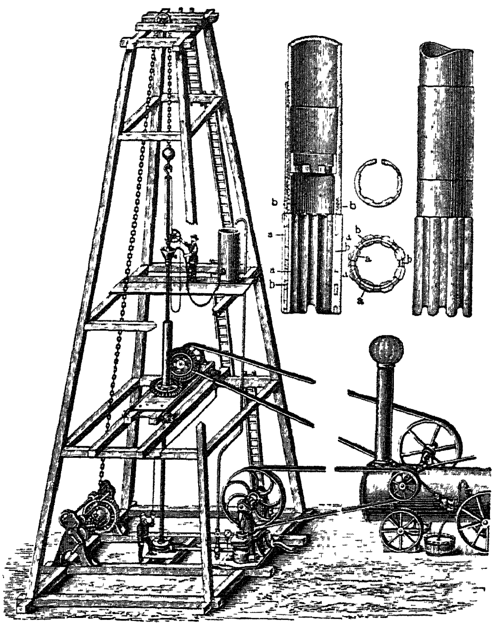


Fig. 80.

From the large reservoir near the wells, the petroleum passes by means of iron pipes to the refineries or to the despatching stations (suitable trains or vessels), which at Baku are very near, but in America some hundreds of kiloms. from the wells; these pipes then traverse plains, mountains, and valleys, and in the same way and with the help of powerful pumping-stations, the refined petroleum is despatched to the place of loading. In 1905, the Standard Oil Company began the construction of another such pipe (*pipe-line*) to connect the works at Kansas City with the coast; the distance is about 1700 miles and the construction cost £880,000 and served to transport daily from 10,000 to 15,000 barrels of petroleum.

[1] Artesian wells for extracting petroleum have an average diameter of 25 to 50 cm., and vary in depth according to the region; at Baku they were first of all 60 to 150 metres deep. But of recent years wells have usually been sunk to a depth of 250 to 350 metres (occasionally 1000 metres). In the Washington district of the United States the wells are from 700 to 850 metres, and near Pittsburg is the deepest of all, 1820 metres. The wells are 100 to 200 metres apart according to the locality, and they remain active for five to ten years.

The expense of boring varies with the district, that is, with the nature of the subsoil, and, under favourable conditions and for wells not too deep, each boring costs about £400. Those made in the Washington district cost even £1400 to £1600. At Velleia in the province of Piacenza, the wells are little more than 100 metres deep, whilst at Salsomaggiore they have been bored to a depth of 400 metres, and in one case of 700 metres, in order to utilise for medical purposes the iodine-salt water which is obtained, together with a little petroleum. In America the

DISTILLATION. Crude petroleum cannot be used as it is for lighting, as it has a bad smell and colour, contains many impurities, and is composed partly of too volatile products, which might easily cause explosions or fires in the lamps. In order to avoid these dangers, the petroleum is subjected to exact refining, which is controlled by legal enactments and with special apparatus (*see later*).

The refining is carried out in a manner which varies with the nature of the petroleum and usually consists of a fractional distillation and a chemical purification. The fractional distillation in the laboratory is carried out in Engler flasks (Fig. 81), which are of definite size and shape and permit of concordant results being obtained in all laboratories; the following fractions are then weighed separately:

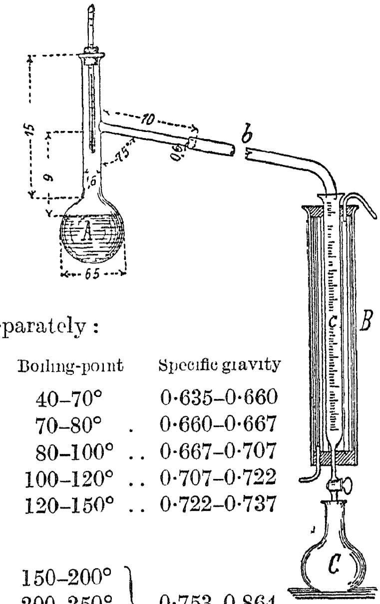


FIG. 81.

	Boiling-point	Specific gravity
I. *Light or readily volatile petroleums*:		
(*a*) *Petroleum ether*	40–70°	0·635–0·660
(*b*) *Gasolene*	70–80° .	0·660–0·667
(*c*) *Benzine*	80–100° ..	0·667–0·707
(*d*) *Ligroin* (burnt in special lamps for lighting)	100–120° ..	0·707–0·722
(*e*) *Petroline* (used for de-fatting or cleaning) .	120–150° ..	0·722–0·737
II. *Petroleum for lighting*:		
I quality	150–200°	0·753–0 864
II quality	200–250°	
III quality	250–300°	
III *Residues of the distillation*.		
(*a*) *Heavy oils*: lubricating oils . .	above 300° ..	0·7446–0·8588
(*b*) *Paraffin oil*		0·8588–0·9590
(*c*) Coke		

The *industrial refining* of petroleum consists in separating the crude petroleum into these three groups, I, II, and III.

Apparatus is used for periodic or alternate distillation, or for continuous distillation.

Periodic distillation is conveniently carried out in the so-called *waggon-still* largely used in America and at Baku. It holds as much as 2500 barrels at a time (Figs. 82 and 83).

It is made of wrought iron 10–14 mm. in thickness, and has a corrugated bottom; it is commonly 7 metres long, 4 metres wide, and 3 metres deep. The top is fitted with three flanged elbows which carry off the vapour. In thirty hours three distillations can be carried through, the residues being discharged through the three orifices, *c*. The heating is effected by means of these residues, which are forced into perforated pipes, *r*, in the double-arched hearth; rational circulation of the products of combustion results in effective utilisation of the heat.

More profitable use is made to-day of simpler, cylindrical boilers, which, although of larger dimensions, correspond almost exactly with the various types of steam-boilers, the heating being external, or lateral, or internal, or two of these together. Such boilers

well is widened at its lowest point, where it meets the petroleum, by exploding a dynamite cartridge ("torpedoing").

A well sunk in 1891 at Balakhany, 270 metres deep, gave an uninterrupted jet producing 3276 tons of petroleum per twenty-four hours, and the mass of sand expelled covered the whole neighbourhood. A little distance away one of the Nobel Company's wells, in 1892, gave 13,000 tons per day. In February 1893 a well was sunk at Romany, near Baku, which for several weeks yielded 10,000 tons of petroleum per day; the oil issued from the earth with such violence that the movement of the air broke the windows of neighbouring houses, and, as at first it was not possible to guide the jet into horizontal channels, all the iron plates used for this purpose being pierced, 250,000 tons of petroleum were lost in five weeks. In 1909 a new well at Baku gave, for a long time, 3500 tons of naphtha per day. A well bored at Maikop (70 kiloms. from the Black Sea), on September 12, 1910, to a depth of 70 metres, gave a jet 64 metres above the surface of the ground and a production of 6000 tons in twenty-four hours; on September 18 the fountain caught fire and five days passed before it could be extinguished.

Fountains as rich as this are exceptional; usually wells yield much less, and at Baku a well is generally abandoned when it gives less than four tons in twenty-four hours. In Italy, however, wells are used which give only a few hundredweights of petroleum per day; some of the Italian wells produce only 60 litres a day, others as much as 2500 litres or more.

of 600–700 or more barrels capacity are commonly used even in America, where, however, both the more complex and more perfect Lugo apparatus and the Rossmässler apparatus, in which the heating is effected by superheated steam, are used.

For the condensation of the vapours that distil over, complicated iron coils are arranged in cisterns through which cold water circulates continuously, the bore of the pipe being 20–25 cm. at first and gradually diminishing to 5–8 cm.

The distillate with specific gravity not exceeding 0·750 and b.pt. 150° forms the crude benzine and is collected and worked up separately. The distillate with sp. gr. 0·750–0·860 forms the lighting oil, and the *residue* is treated separately.

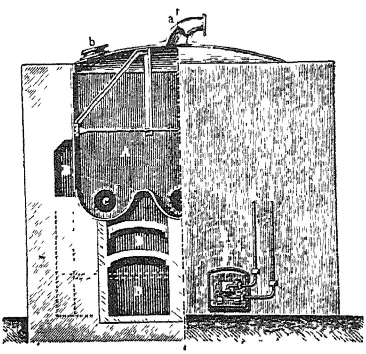


FIG 82.

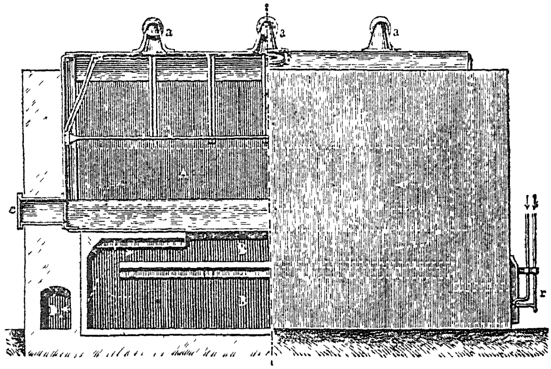


FIG. 83.

Continuous distillation is employed more especially at Baku, with large plants consisting of boilers arranged in series so that each boiler is maintained at a definite, constant temperature, the vapours passing from one boiler to the other only depositing in a condensed form those portions corresponding with a given boiling-point and a given specific gravity. By feeding the first boiler—which is at the highest temperature—continuously, the others are also fed indirectly and kept full, each of them discharging a fraction of a definite, constant specific gravity. Naturally the higher temperature boilers are furnished with *dephlegmators* (Fig. 84), which cause ready deposition of the heavy oil carried over with the very hot vapours. In these boilers the heating or distillation is effected by

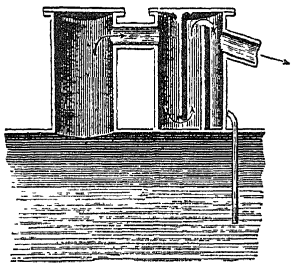


FIG. 84.

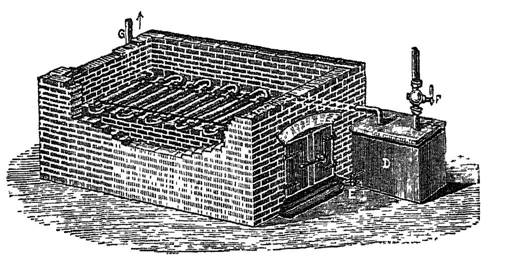


FIG. 85.

means of *superheated steam*, which is usually obtained by passing steam from a boiler (*D*, Fig. 85) through a series of iron pipes heated in a furnace by direct-fire heat.

In addition to other advantages, continuous distillation gives an increase of 30 per cent. in the amount of solar oil. The residue left after distilling the crude petroleum up to 280° bears the Tartar name of *masut* or the Russian one of *astatki* (*ostatki*). The amount of petroleum distilled in twenty-four hours corresponds with four times the capacity of all the boilers in the battery.

The Nobel Company at Baku has boilers which distil 1000 tons of petroleum in twenty-four hours. During recent years rectifying columns similar to those used for alcohol have been employed, these admitting of a large production without the use of large boilers.

In the "Black Town" near Baku, there are 200 refineries which treat the whole of the

petroleum of the district. The odour of petroleum is perceptible at a great distance, and the town is always covered and surrounded with dense, black smoke. The most important refinery is that of Nobel Brothers, which refines half of the annual output of the Caspian, although this firm possesses only one-eighth of the total number of wells.

CHEMICAL PURIFICATION OF PETROLEUM. The petroleum distilling between 150° and 300° is not yet suitable for lighting purposes, as it has a marked, rather unpleasant odour; it has a faint yellow colour, and contains substances which detract from its value. It was Eichler at Baku who first suggested purification by means of concentrated sulphuric acid.

This is carried out in large iron tanks with conical bases (Fig. 86), the petroleum being treated with several separate quantities (altogether 1–3 per cent.) of concentrated sulphuric acid of 66° Bé. (nowadays the monohydrate obtained by the catalytic process), the mixture being vigorously agitated by compressed air blown in at the bottom of the tank, and each quantity of the acid separated after half an hour's rest.

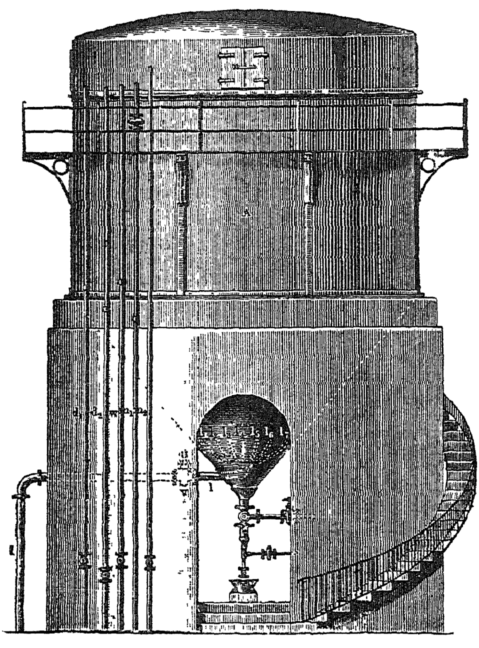


FIG. 86

The sulphuric acid acts especially on the aromatic hydrocarbons (forming sulphonic acids), the olefines and the oxygenated acid compounds, as well as on the colouring and sulphur substances. A small part (1–3 per cent.) of the petroleum is resinified and the acid is turned black, but can still be used for the manufacture of superphosphates.[1] In order to weaken the action of the acid somewhat, it is mixed with sodium sulphate; further, in order that yellowing of the petroleum may be avoided, sulphuric acid containing less than 0·01 per cent. of nitrous acid should be employed. After the action of the acid, the petroleum is washed thoroughly with water and then with 1–1·5 per cent. of concentrated caustic soda solution (30–33° Bé.), air being passed in from beneath to effect mixing; in this way the traces of acid remaining and also the phenolic compounds are removed. After the alkali has been separated, the oil is again well washed with water. The remaining petroleum is not clear, as it is emulsified with a little water, but it clarifies on standing and on being filtered rapidly through sawdust and salt, which remove all traces of emulsion. The alkaline petroleum residues are now used in some places to impregnate and preserve railway sleepers; but sometimes they are subjected to dry distillation, which regenerates the soda and gives coke and unsaturated hydrocarbons and ketones (acetone, &c.). The heating of these alkaline residues also yields naphthenic acids (tridecanaphthenic acid), from which cheap antiseptic soaps are prepared.

Some crude petroleums give a rather yellow solar oil, which is decolorised by exposure for some time to the sun in shallow tanks covered with sheets of glass. Sometimes the yellow tint is removed by dissolving in the petroleum traces of complementary blue or violet dyes; as, however, nearly all commercial dyes are insoluble in petroleum, it is necessary to obtain from the manufacturers the *bases* of these colouring-matters, these being soluble.

In certain cases, decolorisation is attained with infusorial earths, clays, or natural magnesium hydrosilicates.

A most important operation for petroleum rich in *sulphur* (present especially as H_2S)

[1] According to Ger. Pat 221,615 of 1909 this black acid, containing sometimes as much as 2·5 per cent. of complex organic substances, may be purified by causing it to fall into pure, boiling sulphuric acid through which a current of air is passed; all the acid distilling over is then pure and colourless J Fleischer (1907) obtains colourless acid (45° to 50° Bé.) by causing the black acid to diffuse through porous partitions washed by a little water.

and hence dark and of unpleasant odour (like those from Canada, which can be used only as a combustible and not for lighting purposes) is that of a *desulphurising* according to the process proposed by Frasch (1888–1893); this consists in distilling the petroleum with an excess of a mixture of metallic oxides—powdered copper oxide, 75 per cent.; lead oxide, 10 per cent.; iron oxide, 15 per cent. This operation reduces the sulphur-content from 0·75 per cent. or more to 0·02 per cent. It is calculated that, by this method, about 50 tons of sulphur are extracted daily from Ohio petroleum, most of it being lost.

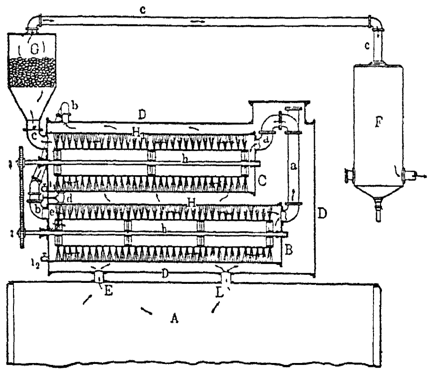


FIG. 87.

The operation is carried out by simple *mixing* or by means of *vapour*. In the first case 6800 kilos (68 quintals) of the oxide mixture are added to 200 tons of petroleum in a large tank, the mixture being subjected to prolonged agitation by mechanical stirrers, which keep the oxidising mass at the bottom of the tank in continual motion.

The petroleum is then decanted off into the fractional distilling apparatus, a second quantity of 200 tons of petroleum, together with 4500 kilos (45 quintals) of oxides being added to the residue in the tank; the operation is repeated four or five times before renewing the oxides completely.

The Frasch process of desulphurising the vapour is far more rational and rapid; it consists in passing the petroleum vapours from the distillation vessel (from 100 tons of petroleum) (*A*, Fig. 87) successively into two communicating cylinders, *B* and *C*, placed one over the other and enclosed by a metal casing, *D*, above the boiler. The vapours pass first into the casing, next into the lower cylinder, and then into the upper one, coming into intimate contact with the mixture of metallic oxides, which are kept moving and subdivided in both cylinders by means of rotating reels, *h*, provided with peripheral brushes, *H*. The oxidising mixtures in the two cylinders are renewed alternately, while the purified vapours, after traversing a gravel filter, *G*, which retains particles of the oxides carried over, are condensed in ordinary coils, *F*. By this process, some refineries are able to purify as much as 11,000 tons of petroleum per day.

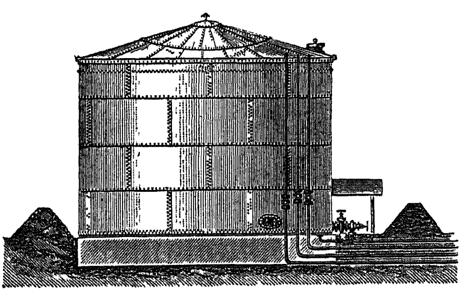


FIG. 88.

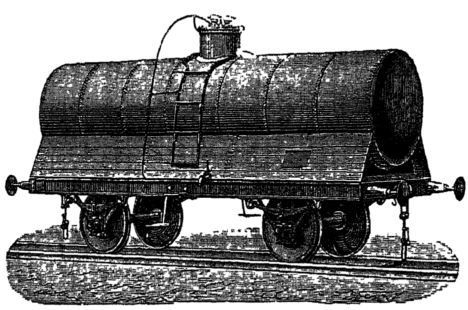


FIG. 89.

Recently petroleum has been desulphurised by means of metallic sodium, and treatment with aluminium chloride in the hot and under pressure is also recommended. V. Walker (U.S. Pat. 955,372, 1910) passes the vapours into columns fitted with perforated plates and containing anhydrous cupric chloride, the last traces of hydrogen sulphide being removed by passing the vapours into a solution of lead oxide in caustic soda. Robinson (1909) separates the sulphur by treating the petroleum with highly concentrated sulphuric acid.

In well-refined petroleums, the proportion of sulphur is always less than 0·06 per cent., usually 0·02 per cent.

PETROLEUM TANKS. The refined petroleum is preserved in large cylindrical sheet-metal tanks (Fig. 88), situated near the works; they are whitened outside to reflect

the heat of the sun, and are furnished with charging and discharging pipes communicating with the pumping-station by which all the liquids in the works are circulated.

For transport by land and sea, wooden casks holding 159 litres (about 145 kilos) were at one time exclusively used, but to-day land transport is effected by tank-cars (Fig. 89), which are now numbered in hundreds of thousands. For sea transport, tank-steamers are used (there are now 360 of these of the total capacity of 630,000 tons) (Fig. 90); when they arrive at their destinations in the ports of different countries, they are discharged by means of pumps into storage-tanks or directly into tank-cars. From these stores (there are tanks of 2000 tons capacity at Leghorn, Savona, Genoa, and Venice) it is dispatched inland in wooden or iron casks or in cans holding 14 kilos (17 litres) and packed in pairs in wooden cases.

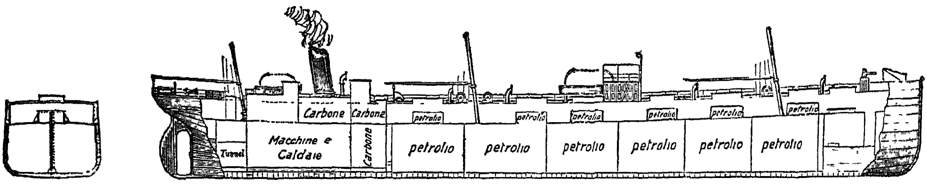


FIG. 90

Carbone, coal; *petrolio*, petroleum; *macchine e caldaie*, engines and boilers.

USES AND STATISTICS. The greater part of refined petroleum is still used for lighting purposes, either in the old lamps with flat wicks or in those with cylindrical wicks and flame-spreaders or in lamps with incandescent Auer mantles; it can be used advantageously for household illumination in town and country. Part of it is employed for power purposes, as in internal-combustion engines it gives an efficiency of 25–37 per cent., whilst coal yields only 12 per cent. However, while in Russia large quantities of petroleum were used in the past in factories and for locomotives, nowadays it is being replaced by coal; in America, on the other hand, the opposite is the case, and the Mexican Railway alone consumed more than 4000 barrels of petroleum per day for its locomotives in 1908. Its use on fast ships has the advantage of 28 per cent. saving in space. In America, about 19,000,000 barrels of petroleum were used altogether for railway locomotives in 1907. Lastly, it is used as a disinfectant and for lubricating engines, &c.

The *production* of petroleum has increased in a surprising manner, in spite of the growing development of the gas and electrical industries. The following figures illustrate this for the two great petroleum-producing regions:

	Caucasus (Russia) Tons	United States Tons
In 1874	100,000	1,500,000
1884	1,500,000	3,400,000
1894	5,000,000	7,000,000
1903	9,902,000	13,160,000
1905	7,969,239	17,636,000
1908	8,292,000	23,940,000
1910	9,500,000	26,000,000

In America to-day petroleum is monopolised by huge "trusts," especially the Vacuum Oil Company and the Standard Oil Company of New Jersey, to which are affiliated seventy companies with a total capital of £18,000,000 and employing 60,000 workmen and monopolising about 60 per cent of American petroleum. The Standard Oil Company, founded in 1872, paid in dividends from 1882 to 1892 a total of £94,400,000, and from 1894 to 1903 paid to its shareholders dividends of 33 to 48 per cent.! In 1906 President Roosevelt, under pressure of public opinion, waged war against this colossal trust by rupturing the connection between the steel ring and the interests bound up with it and making them liable to a fine of over £6,000,000. In consequence of this commercial war of 1906 the Standard Oil Company lost £25,000,000, of which £12,900,000 fell on Rockefeller, the well-known millionaire president of the company. The sentence was then annulled on appeal, but the result was that the company fought its competitors by lowering prices (petroleum that previously cost 30 centesimi (2 9*d*) per litre has been lowered in price during the last few years to 15 centesimi (1·45*d*.)), and in 1908 made a net profit of £16,000,000, and proposed raising its capital to £100,000,000. This explains how Rockefeller has been able, without any great sacrifice, to make benefactions of so many millions during the past few years, especially for the extension of university study in America. The last sentence of the Supreme Court of Washington (May 15, 1911) gave judgment against the Standard Oil Company, for contravention of the law against trusts, and ordered dissolution of this powerful company within six months

One-third of the American production has been given by California, more than one-fourth by Texas, and one-sixth by Ohio, and now one-sixth is given by Illinois, one-fourth by California, and one-fourth by Oklahoma. In 1910 the Californian production reached almost 10 million tons.

The total *production of the world* was about 12,000,000 tons in 1894, 31,000,000 in 1905, and 38,000,000 in 1908. The following Table gives, in the first three columns the production in thousands of tons of each of the petroleum-producing countries of the world, and in the last three columns the percentages of the total amounts yielded by each country :

				Per cent of the total production		
	1903	1905	1908	1900	1902	1908
United States . .	13,600	20,000	23,940	51·50	52·51	63·0
Russia . . .	9,902	7,969·2	8,292	42·41	37·12	21·8
Dutch East Indies .	870	1,126 3	1,143	1·83	3·50	3·0
Galicia . . .	728	835 8	1,754	1·97	2·90	4·6
Roumania[1] .	381	641·0	1,148	0·85	1·74	3·0
British India .	329	599·8	672	0·87	1·42	1·7
Japan . . .	126	194·4	276	0·86	0·50	0·75
Canada . . .	—	91·9	70·5	0·18	0·24	0·20
Germany . .	58·9	81 3	141·9			0·35
Italy . . .	2·5	6·1	7·08			0·02
Peru . . .	—	5·4	135			0·35
Various other countries	79·0					

In 1890, Germany produced only 15,000 tons of crude petroleum.

The country that consumes the most petroleum, after the United States and Russia, is Germany, where, in 1904, 970,600 tons were used for lighting, 143,000 tons for lubricating purposes, and 110,000 tons for various other uses ; in 1909, it imported about 950,000 tons of refined petroleum and 31,400 tons of crude petroleum, of a total value of £3,600,000.

The importation into Italy has been as follows :

	1884	1890	1900	1904	1906	1907	1908	1909	1910
Tons .	73,361	72,000	73,000	69,233	61,588	72,714	82,373	88,930	84,748

and whilst in 1907 two-thirds of this came from the United States, one-fourth from Russia, and little from Roumania, after the new commercial treaty with the last two nations, the proportions changed considerably, Roumania alone sending 29,000 tons in 1909.

Almost the whole of the Italian industry is in the hands of one company, and the production is very small and almost stationary.

The consumption of petroleum by different countries is quite different proportionately from the production, as is shown in the following Table, which gives the mean consumption per inhabitant in 1904 :

	Total consumption Tons		Annual consumption per inhabitant Kilos
United States	2,016,700	..	25·21
Germany	970,600	..	16·72
England	520,933	..	11·84
France	312,210	..	8·22
Russia (140,000,000 inhabitants) . .	1,050,787	..	7·51
Japan	299,370	..	6·65

[1] In 1910 the production was 1,352,300 tons, 339,300 tons of distilled petroleum and 125,750 tons of benzine being exported. In 1903 the refineries of Roumania treated altogether 314,748 tons and in 1904 391,387 tons of crude petroleum, which yielded 62,218 tons of benzine, 109,510 tons of lighting oil, 30,214 tons of mineral oil, and 173,661 tons of residues. In 1909 Roumania exported 420,000 tons of petroleum benzine, and mineral oils.

	Total consumption		Annual consumption per inhabitant
	Tons		Kilos
Roumania	27,025	..	4·50
Austria-Hungary	215,546	..	4·31
Italy	73,000	..	2·21
India (300,000,000 inhabitants)	503,930	..	1·70
China (300,000,000 inhabitants)	254,464	..	0 85

The *units of measure* of petroleum in different countries have already been given on p. 58.

In view of the enormous and increasing consumption of petroleum, it may be interesting to know how much longer the known stock of petroleum in the earth will last. According to the calculations made in 1909 by the Geological Survey Office, the known deposits of petroleum would last until 1990 if the annual consumption remained at its present amount, but if the consumption increases in the same proportion as it has been doing during the last few years, the deposits will be exhausted in 1935.

The price of rectified petroleum at Batoum is about 7*s.* 2*d.* per quintal, and the transport to Genoa 1*s.* 5*d.*, and, making allowance for all taxes, Russian petroleum costs at Genoa 16*s.* per quintal, including the cask; the American costs 16*s.* 10*d.*, and at the present time Russian petroleum is beginning to oust the American product from the European markets. In the free port of Hamburg, Russian and American petroleums cost 16*s.* 10*d.* per quintal in 1879, 13*s.* 7*d.* in 1890, and 14*s.* 9½*d.* in 1904.

TESTS FOR LIGHTING PETROLEUM. A good petroleum is limpid and colourless, does not turn brown with sulphuric acid (sp. gr. 1·53), and has a specific gravity of 0·820–0·825 (Russian) or 0·780–0·805 (American); the specific gravity is determined with an aerometer at 15° (corrected by 0·0007° for each degree) and referred to water at 4°. It should not have an acid *reaction*; when 10 c.c. of the petroleum is dissolved in a mixture of alcohol and ether previously rendered neutral to phenolphthalein, an immediate violet coloration should be produced on addition of a single drop of N/10 alcoholic caustic soda. When subjected to *fractional distillation* in the Engler flask (p. 66), it should not yield products distilling below 110°, only 5 per cent. or at most 10 per cent. up to 150°, and less than 10 per cent. or at most 15 per cent. above 300°; in the distillation products the difference in specific gravity between Russian and American petroleums is increasingly marked. American petroleum is distinguished from the Russian (*see* p. 62 *et seq.*) also with the *refractometer* and by the different solubilities of the fractions of equal specific gravity in a mixture of chloroform and aqueous alcohol (Riche-Halphen test)[1]. The *viscosity* determined with the Engler viscosimeter (*see later*, Mineral Oils) should not be greater than 1·15 at 20°. The luminosity is determined with the Bunsen photometer (p. 56) and, in general, 3·5–5 grms. are consumed per candle-hour.

The determination of the temperature at which a petroleum gives off *inflammable vapours* is of great importance, and in order to obtain concordant results, the Abel apparatus modified by Penski (Figs. 91 and 92) is employed in all laboratories. The petroleum to be examined is placed in a brass receiver, *G*, up to the level-index, *h*; the cover, *D S*, carries a thermometer, *t*, which dips into the petroleum, and a clockwork mechanism, *T b*, which, when it is released (by a lever, *h*), opens automatically a small window in the cover; at the same instant a small oil-flame passes through the window and is immediately withdrawn, the window then closing. The petroleum receiver is surrounded by an air-chamber, *A*, which is heated to 55° in the reservoir, *W*, regulated by the thermometer t_2. For every 0·5° increase of temperature of the petroleum, the spring is released, this being continued until the flame ignites and explodes the mixed petroleum vapour and air. The slight explosion sometimes extinguishes the flame. The temperature shown at this

[1] Of each fraction with specific gravity higher than 0·760, 4 grms. is weighed into a beaker, and from a burette a mixture in equal parts of anhydrous chloroform and 93 per cent. alcohol is run in until the turbidity first formed suddenly disappears:

Density	0·760	0·770	0·780	0·790	0·800	0·810	0·820	0·830	0·850	0·880
American petroleum (cubic centimetres solvent)	4·3	4·6	5·2	5·9	6·6	7·7	9·5	11 3	—	—
Russian petroleum (cubic centimetres solvent)	4·0	3·8	4·1	4·2	4·0	4·2	4 5	5·0	6·4	11·9

Italian petroleums behave like the Russian, but this reaction does not serve to distinguish between the other European petroleums (Utz, 1905).

moment by the thermometer t_1 is that of inflammability (*flash-point*), which is, however, influenced by the atmospheric pressure and should be corrected by $+ 0{\cdot}035°$ for every mm. of pressure above 760 mm.

In Italy, Germany, and Austria the sale of petroleum for lighting purposes is prohibited if it shows a flash-point below 21° in the Abel apparatus ; otherwise explosive vapours could be formed in ordinary lamps, even at 30° or 32°, which would be dangerous. A petroleum inflammable at above 60° (Abel) cannot be used for lamps.

A rough-and-ready test to detect if a petroleum is dangerous consists in pouring a little into a glass and throwing into it a lighted match ; if the latter is extinguished, the petroleum is safe.

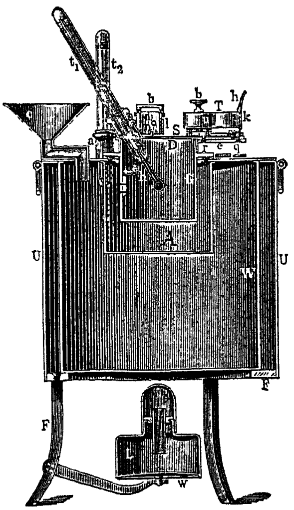


FIG. 91.

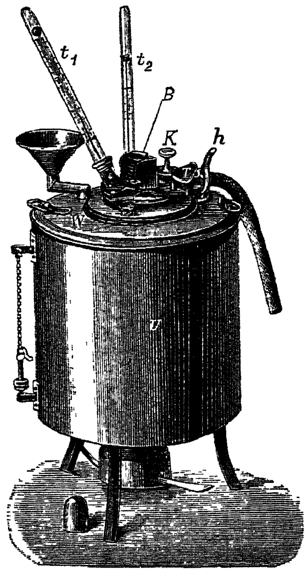


FIG. 92.

The *illuminating power* is determined with the Lummer and Brodhun photometer (*see* Fig. 77, p. 56). To determine the *moisture* or *water*, which does not separate well in the distillation of certain Californian petroleums, Robert and Fraser (1910) proposed adding calcium carbide and measuring the quantity of acetylene formed, this depending on the amount of water present.

TREATMENT OF CRUDE BENZINE

The portion of crude petroleum distilling below 150° forms crude benzine, which can be separated by fractional distillation into various qualities for different commercial uses.

The crude benzine is redistilled in small horizontal or vertical boilers, usually heated by superheated steam either in a jacket or in closed coils inside the boiler, the condensed water being collected outside the boiler.

In some cases moderate fire-heat is used in addition.

When there are many volatile products, an apparatus similar to that used in the rectification of spirit is employed. Such a system of rectifying columns is to-day in general use, and the condensation of the vapours and the cooling of the condensed benzine are effected by the crude benzine, which is thus fractionated and fuel at the same time economised.

A special apparatus for condensation and rectification, devised by Veith, consists of five iron double-walled cylinders (with water-circulation), connected in series and terminating in a sixth cylinder containing a coil with many turns for the condensation of the vapour from the preceding cylinder. The coil is cooled by ice and cold water, which then passes successively into the jackets of the other five cylinders and gradually becomes heated. These five cylinders are full of pure iron turnings free from oil. The vapours from the boiler in which the benzine is distilled pass through cylinders 1–5, in each of which

that part condenses which is liquefied at the temperature of the water circulating in the jacket.

The least volatile products condense in the first cylinder and the most volatile ones in the final coil. At the bottom of each cylinder is a pipe with a tap communicating with a tank.

The apparatus for distilling and rectifying benzine are so constructed that the vapour above the boiling liquid which is mixed with air is separated from the liquid, *e.g.* by metal gauze, so that in case of fire or explosion the liquid does not ignite.

Baku petroleums give only 0·2 per cent. of benzine, those of Grosny (Russia) about 4·5 per cent. In 1902, 341,000 tons of naphtha were distilled at Grosny, 14,000 tons of benzine (about 4 per cent.) being obtained. Pennsylvanian petroleums give up to 12 per cent. of benzine, and those from Campina (Roumania) 3–5 per cent.; a petroleum from Anapa (Caucasus) gave 28 per cent. Italian petroleums from Emilia yield 30–35 per cent. of benzine.

After the fractional distillation of the benzine the separate portions are often refined by treating with concentrated sulphuric acid mixed with 0·2 per cent. of potassium dichromate and 0·01 per cent. of lead oxide. Fuming sulphuric acid also gives good results, but animal charcoal and magnesium hydrosilicates are not very satisfactory. The treatment is carried out in closed vessels with mechanical stirrers, the use of compressed air being inapplicable here.

The majority of the benzine is produced at Baku and in Pennsylvania, but some is refined in Germany and large quantities are sent to Europe from the East Indies—from Java, Sumatra, and Borneo; Galicia and Roumania also yield large quantities.

The consumption of benzine is to-day tending to increase, not only as a solvent for fats (benzine boiling between 60° and 80°), but also for automobiles, aeroplanes, and dirigible balloons, its calorific value (about 11,000 cals.) being high. That used for cleaning fabrics should boil at a higher temperature, otherwise it evaporates too easily and leaves an annular mark round the spot (other varieties, *see* p. 66).

The consumption of benzine in the various countries of Europe amounted in 1908 to: 115,000 tons in Germany, 130,000 tons in France, 100,000 tons in England, 10,000 tons in the Netherlands, 110,000 tons in Russia, 20,000 tons in Roumania, 10,000 tons in Austria and Galicia, and 25,000 tons in other European countries. The United States produced 800,000 tons of benzine in 1908 and the Dutch Indies 260,000 tons.

TREATMENT OF PETROLEUM RESIDUES

A. Lubricating Oils. *B*. Vaseline. *C*. Paraffin.

(*A*) LUBRICATING OILS. The crude petroleum residue remaining in the boilers at 300° (astatki or masut [1]) forms a brownish black mass with a greenish reflection, dense and sometimes semi-solid at ordinary temperature, and often with a burnt, faintly creosotic smell; it has a specific gravity of 0·900–0·950 and a coefficient of expansion of 0·00091, and gives inflammable vapour even at 120–160°; that of Baku contains no paraffin and hence does not freeze. When these residues are discharged from the boiler, in order to cool them and so prevent them taking fire they are passed through the tubes which serve to heat the crude petroleum before introducing it into the boiler. At Baku the residues, which form almost two-thirds of the crude naphtha, are largely used as a combustible for the distillation vessels and also for locomotives and marine engines, the calorific power being 9700–10,800 cals. and 1 kilo being able to evaporate as much as 14–15 kilos of water.[2]

[1] *Masut* contains, on the average, 87·5 per cent. C, 11 per cent H, and 1·5 per cent. O; it has a mean specific gravity of 0 91, an ignition temperature of 110° and a calorific value of 10,700 cals When used as a combustible it is gasified, the vapours, mixed with compressed air, burning completely, it is often burnt directly after pulverisation with compressed air or steam.

In view of the great calorific value of petroleum residues and their increasing production, new outlets have been sought for them; they should have a great future as a substitute for coal in the heating of boilers, steam-engines, ships, &c.

But, as has been already stated, this use of it is diminishing in Russia, although continually extending in the United States. In Italy attempts have recently (1911) been made to burn it, after pulverisation, directly under boilers, and it can be used advantageously if it does not cost at the factory more than about 5*s.* per quintal, coal giving 8000 cals. costing 2*s.* 10*d.*; the cost of transport is hence excessive, increasing the price from 10*d.* or 15*d.* at the refinery to 5*s.* in Italy. The Customs duty (Italy) is 20 centesimi (just under 2*d.*) per quintal.

The heavy oils extracted from petroleum residues are largely used for special engines of the Diesel type.

[2] "Cracking" Process. In some cases it is convenient to convert the heavy mineral oils (and also the *masut*) into petroleum for lighting, use being made of the process of *cracking*. This is based on the fact,

Utilisation of a great part of these residues was commenced after the first American and Scotch samples (from shale oils) were exhibited at the International Exhibition at Paris in 1867. In Russia enormous quantities of residues, of almost no commercial value, accumulated every year. Their utilisation was initiated in 1876 by the Ragosin process for preparing the best lubricating oils (those of Baku are highly valued) by distilling the residues by means of superheated steam, so as to avoid the formation of empyreumatic odours.

The distillation is now carried out in long horizontal boilers, since in vertical ones—which were used at one time—the vapours, in contact with the heated walls, give products of profound decomposition and of bad odour. Direct-fire heating can be partly used in conjunction with internal heating by superheated steam at 220°, and the distillation is facilitated by carrying it out in a vacuum.

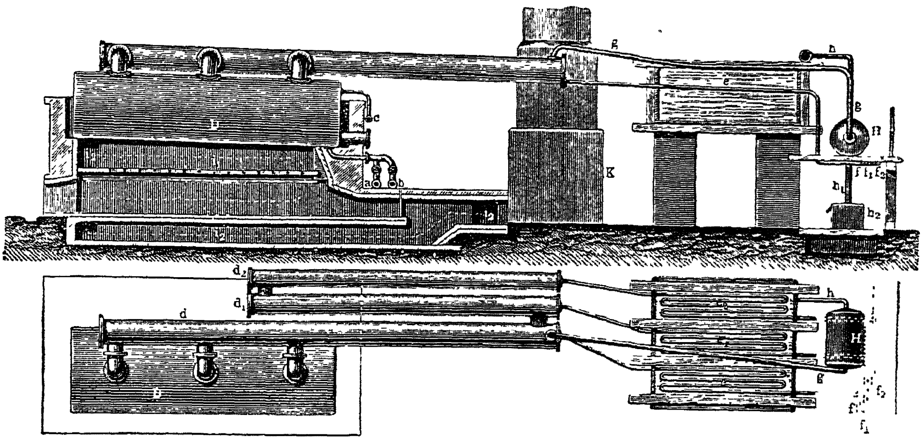


FIG. 94.

Fig. 94 shows the plant used by Nobel Brothers at Baku. The condensation is effected in long, parallel, slightly slanting pipes, d, d_1, d_2 (40–50 cm. in diameter), communicating alternately at the ends. The first of these is cooled by air alone, the second by water and the third by very cold water that circulates in a coil; H is an exhaust-pump. At

established in 1872 by Thorpe and Young, that, when the vapours of heavy petroleums are superheated, they yield gaseous hydrocarbons (6 to 8 per cent.) poorer in hydrogen (ethylene series) and lighter liquids which can be used as second quality petroleum. The operation is carried out in a vertical boiler (Fig. 93), placed in a furnace so that its walls are strongly heated by the hot fumes circulating round them. The boiler is not completely filled with masut, so that the vapours evolved, coming into contact with the red-hot walls above the liquid, are decomposed; after separation in a dephlegmator of the heavy oil carried over, the vapours are progressively liquefied in ordinary condensers or refrigerators, yielding solar oil, benzine, &c., whilst the remaining gas is used for heating or for gas engines. A mineral oil from Ohio treated by this process gave the following products: 25 per cent. of benzine (sp. gr. 0·650–0·745), 33 per cent. of lighting petroleum (sp. gr. 0·800–0·840), 10 per cent. of light paraffin oils for burning (sp. gr. 0·854–0·859), 31 per cent. of solid paraffin and paraffin oil (sp. gr. 0·870–0·925), and 3 per cent. of coke and loss.

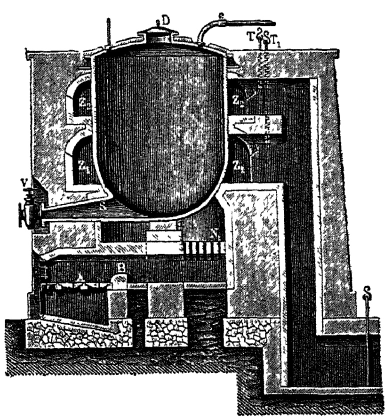


FIG. 93.

Manufacture of Benzene from Naphtha. Attempts in this direction had already been made as early as 1875, and later Ragosin and Nikiforow, Krey, Laing, Dewar, and Redwood attacked the problem, but without practical success. Recently Nikiforow appears to have succeeded and he has devised a plant for treating 2400 tons of naphtha and producing 262 tons of benzene. He subjects the naphtha to two distillations under different pressures, in a retort first at 500° and then at 1000°. In this way 33 per cent. of tar containing 50 per cent. of aromatic compounds is obtained, together with an abundant supply of gas which serves for heating, lighting, and power purposes. After redistillation and rectification of the first of these products, a final yield of 12 per cent. of benzene and toluene is obtained, 3 per cent. of naphthalene, 1 per cent. of anthracene, and various secondary products. Benzene thus prepared will apparently cost 20s. per quintal and the aniline oil (used in dyeing) obtainable from it would cost about one-half as much as that on the market in Russia. J. Hausmann (Ger. Pat. 227,178, 1909) also obtains benzene and its derivatives by passing the vapours of mineral oil into red-hot tubes, and into contact with catalytic agents (oxides of iron, lead, and cerium, sulphate of iron, &c.).

the bottom of each of these pipes is a discharge pipe for the mineral oil condensates, which pass to water-separators ; thus three qualities of oil are obtained in three separate tanks : 20–25 per cent. of solar oil, specific gravity below 0·890 ; 6–10 per cent. of spindle-oil of sp. gr. 0·890–0·900 ; 25–30 per cent. of engine oil, sp. gr. 0·900–0·920, 3–4 per cent. of cylinder oil, sp. gr. 0·925 ; 3 per cent. of tar ; and 5 per cent. of loss. The quantity of steam consumed varies from 100 to 150 per cent. of the amount of oil distilled and the quantity of masut treated every 24 hours corresponds with about double the volume of the boilers.

A somewhat different apparatus which has also given good results for the *distillation of tar* and of its heavy oils is that made by the firm of Hirzel in Leipzig. The large boiler, *BV*, with a convex base (Figs. 95 and 96) is divided longitudinally by a metal partition, 1, which allows the two halves of the boiler free to communicate at the end, 7 ; the distillation products enter at the tube 4, connected with the horizontal pipe 5, from which the liquid descends to the bottom of the first half of the boiler along the tubes 6 ; the superheated steam enters by the tube 3, which is forked half-way down the boiler and connects with a battery of horizontal perforated pipes running along the bottom of the boiler. The liquid moves slowly in a comparatively thin layer from the first to the second half of the boiler, pass-

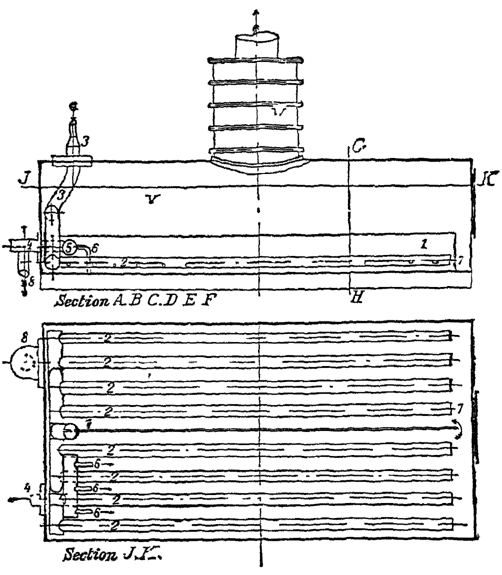


FIG. 95.

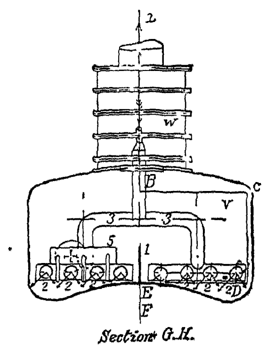


FIG. 96.

ing through the space 7, and issuing at the tube 8 ; the vapours are collected in the dome, *W*, containing perforated discs to condense the drops carried over with the vapours, the latter proceeding through the tube *a* to the rectification or fractional distillation apparatus. In 1911 the Hirzel apparatus was also used by a large Italian firm of metallurgical coke manufacturers and tar distillers.

All these crude mineral lubricating oils, after being freed from moisture by heating, are refined by prolonged shaking with 5–10 per cent. of concentrated sulphuric acid and, after decantation of the black acid, with a concentrated caustic soda solution (15° Bé.) at 60–65°, this being followed by washing with hot water. In these refining operations 8–15 per cent. of the mineral oil is lost. The residues in the boilers, if they are not solid coke, but pasty, are dissolved in benzene as a black varnish for iron, or are used as an adhesive in the manufacture of briquettes from coal-dust, or as a combustible.

According to Ger. Pats. 161,924 and 161,925, it is proposed to treat crude mineral oils with a saturated solution of sodium chloride and carbonate, to blow air in for some time, and finally to distil in presence of an oxide of manganese.

To render mineral oils *inodorous*, or nearly so, they are treated in the hot with formaldehyde, and, after addition of alkali or acid to the mass, a current of steam is passed through (Ger. Pat. 147,163). According to Ger. Pat. 153,585, the 20 per cent. of crude mineral oil is distilled with superheated steam at 180° in presence of 1 per cent. of aqueous lead acetate solution. The distillate is free from sulphur and forms a lighting or gas-engine oil ; the residue, after filtration, forms a denser and almost odourless lubricating oil. In some cases petroleum is *deodorised* by agitating with calcium chloride and a small quantity

of hydrochloric acid, decanting it, shaking with lime to fix the chlorine, and sometimes adding a little amyl acetate or essence of fennel; treatment with soda lye is also resorted to, and, better still, both for mineral oils and petroleums, with sodium peroxide.

Latterly, *mineral oils soluble in water* have acquired importance for lubricating machinery, for greasing textile fibres to be combed, and for watering the streets to prevent dust. They are prepared by the Boleg process (Ger. Pats. 122,451, 129,480, 148,168, 155,288): the mineral oil is heated in a closed vessel, fitted with a condenser, at a temperature of 60–70° or above by means of indirect steam; at the same time finely divided compressed air, after addition of a little caustic soda solution, is injected; a small quantity of resin soap or a sulphoricinate is subsequently introduced, the air-current being continued meanwhile, and finally the whole mass is heated under pressure in an autoclave.

Emulsions of mineral oils with water are obtained by addition of pyridine or quinoline bases or amino-acids.

To obtain from dark mineral oils less coloured oils, and in some cases oils as colourless as water (*e.g. vaseline oils*), the oil is passed slowly through wide, shallow (about 30 cm. deep) filters, filled with a special American clay (fuller's-earth from Florida) consisting of aluminium and magnesium hydrosilicates, previously subjected to slight roasting. The slow filtration is repeated several times and completed in filters arranged in series. The mineral oil remaining in the filters is recovered by displacing it by heavy tar oil (very cheap) and displacing the latter with water. *Decolorisation* is also effected with bone-black or, best of all, by residues from the manufacture of potassium ferrocyanide, which exhibit very great decolorising power (50 per cent. more than American clay); owing, however, to the new methods of manufacturing ferrocyanide, these residues are becoming scarcer and more expensive (they contain 30 per cent. of animal charcoal, considerable quantities of silica and silicates and a little ferric oxide). The darker mineral oils are partly decolorised with sulphuric acid, sometimes together with dichromate.

Carts are often greased with the so-called consistent fats obtained by mixing 15–23 per cent. of calcium soaps and mineral oils with 1–4 per cent. of water (if there is no water the mass remains liquid, and if there is not a little free fatty acid emulsification ceases after a time and the calcium soap separates).

In 1909 Germany imported 216,987 tons of mineral oils. Italy in 1903 imported 24,387 tons of mineral oils (exclusive of petroleum) for engines and steam cylinders, and in 1909 the importation (including a little heavy resin and tar oils) was 43,360 tons of the value of £450,000, besides 8800 tons of residues from the distillation of mineral oils (masut), worth £14,000 (in 1907, 560 tons); in 1910, 49,181 tons were imported. In 1910 England imported mineral lubricating oils to the value of £1,705,366 and mineral oils for gas-engines to the value of £262,455.

REQUIREMENTS IN AND ANALYSIS OF LUBRICATING OILS. Lubricating oils serve to diminish the friction between metal surfaces in motion; by adhering strongly, although in very thin layers, to these surfaces they prevent contact between them and hence friction and heating without sensible increase of the resistance owing to the internal friction of the oil. Lubrication is due partly to chemical phenomena (formation of metallic soaps) and partly to physical phenomena not well understood; in general, where there is much pressure the viscous oils are suitable, and in other places liquid oils, although in practice mixtures of these two kinds are advantageously employed. Oil for lubricating steam cylinders at high temperatures should be resistant to great heat and to the mechanical and chemical action of steam, and should not give inflammable products at a lower temperature than 320°, or 300° where superheated steam is employed; it should possess great adhesive power and viscosity and should not contain resinous or tarry residues. No oil resists the action of steam at above 350°. The good qualities, which are more or less dark, are transparent in the liquid state. The selection for steam cylinders of oils viscous at ordinary temperatures is unimportant, as they become as liquid as water when hot; this is seen from a comparison of the following two mineral oils, the numbers giving the viscosity in seconds required for the passage of 200 c.c. of oil through the Engler viscosimeter (*see later*).

	at 70°	at 100°	at 150°	at 170°
Viscosity of sample I	270	116	74	67
„ „ II	835	226	93	73

The Russian engine oils are more viscous than the American, but the American cylinder oils are more viscous than the Russian. American oils with sp. gr. 0·908–0·920 and 0·844–0·899 have viscosities almost the same as those of the Russian oils with sp. gr. 0·893–0·900 and 0·900–0·923 respectively.

The specific gravities of certain American and Russian oils are as follow:

	American	Russian
Axle oil	0·908–0·911	0·893–0·895
Pale engine oil	0·920	0·903–0·905
Dark engine oil	0·884	0·900–0·920
Cylinder oil	0·886–0·899	0·911–0·923

At the foot of the page is given a summary of the criteria laid down by Holde for various lubricating oils of good quality and the requirements to be answered by those supplied to the Italian railways.[1]

Sometimes mineral oils are used in special motors for utilising their high calorific value (10,500–11,700 cals.). Sherman and Kropf (1908) found that the calorific value of

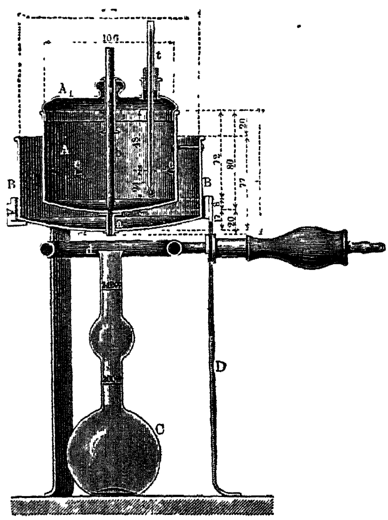


FIG. 97.

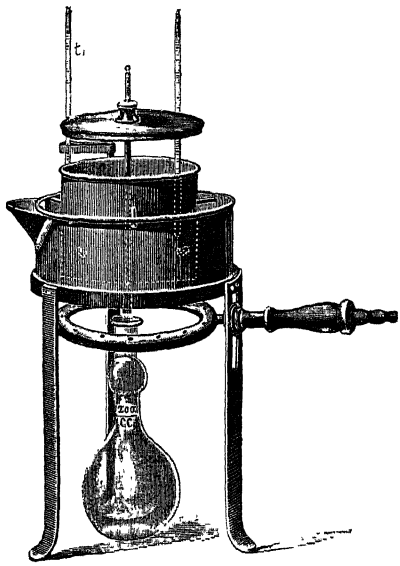


FIG. 98.

mineral oils, and to some extent of petroleums, is inversely proportional to their specific gravity.

The origin and properties of certain mineral oils is sometimes related to their content of paraffin, the *determination* of which is described on p. 86.

[1] (1) *Oil for spinning spindles.* Clear liquids, viscosity (*see later*, Engler viscosimeter), 5 to 12 at 20°, inflammability (in the Martens-Pensky apparatus), 160° to 200°. (2) *Oil for ice-machines or compressors.* Very fluid; viscosity, 5 to 7 at 20°; freezing-point below −20°; inflammability, 140° to 180°. (3) *Oil for light engines and transmission, motors, dynamos.* Medium fluidity, viscosity, 13 to 25 at 20°; inflammability, 160° to 210° (4) *Oils for heavy engines and transmission.* Dense; viscosity, 25 to 45 to 60 at 20°; inflammability, 160° to 210°. (5) *Dark oils for locomotive and railway carriages.* Viscosity, 45 to 60 (summer), 25 to 45 (winter); inflammability above 140°; freezing-point, −5° (summer), −15° (winter) (6) *Oil for steam cylinders.* Very dense or buttery; viscosity, 23 to 45 at 50°; inflammability, 220° to 315°. For these buttery oils, the *dropping-point* is determined by the *Ubbelohde apparatus* (p. 6).

The authorities of the Italian railways demand Russian oils, since these freeze only below −10°, whilst the American ones solidify at 0°; they must not contain water, that is, they must not froth if heated to 129°; they must give no deposit even after standing for forty-eight hours; the viscosity must be at least eight times that of water, they should be perfectly neutral and should not contain shale oil, resin oil, or animal or vegetable oil; they should not have the slightest "drying" properties in the air (smeared on glass), or have a density below 0·91 or a flash-point below 150°–180°; they must not contain more than 10 per cent. of light oils distilling below 310°; when shaken with water, the oil should separate immediately without the water remaining whitish.

With *mineral oils for automobiles* it is important to test for *resin oils*, the procedure being as follows: 5 grms. of the oil are heated with 25 grms. of 60 per cent. alcohol to 40–50° on a water-bath, the mixture being well shaken until it emulsifies, allowed to cool and filtered. The alcohol is driven off from the filtrate on a water-bath and the cold residue treated, drop by drop, with 2 to 3 c.c. of dimethyl sulphate. if resin oil is present, a red coloration is produced.

For lubricating oils it is important to determine the *viscosity*, and this is usually effected by means of the Engler *viscosimeter* (Figs. 97 and 98), formed of a brass vessel, A (sometimes gilt inside), provided with a cover, A_1, through which passes the thermometer, t; at the bottom of the vessel is a platinum tube, a, 20 mm. long and of such dimensions that it allows of the efflux of 200 c.c. of distilled water at 20° in 52–54 secs.; the aperture can be closed from above by the hard wooden peg, b. The vessel, A, is contained in larger one, B, and the space between the two is filled with water maintained constantly at the desired temperature by means of the ring-burner, d, and the thermometer, t_1. The dimensions of the apparatus are exactly defined and are shown in millimetres in the figure. The mineral oil is introduced into A (clean and dry) up to the level indicated by the three points (about 240 c.c.). When the temperature of the oil in A has the desired constant value, the flask C is placed under the efflux tube and the peg rapidly removed, the exact number of seconds taken to fill the flask to the 200 c.c. mark being determined by a chronometer. The time required, in seconds, divided by the corresponding number of seconds for water at the same temperature gives directly the *degree of viscosity*.

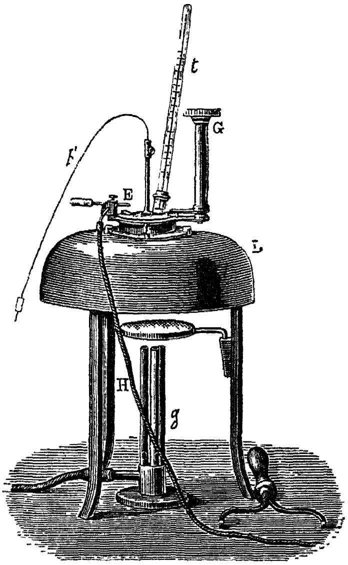


FIG. 99.

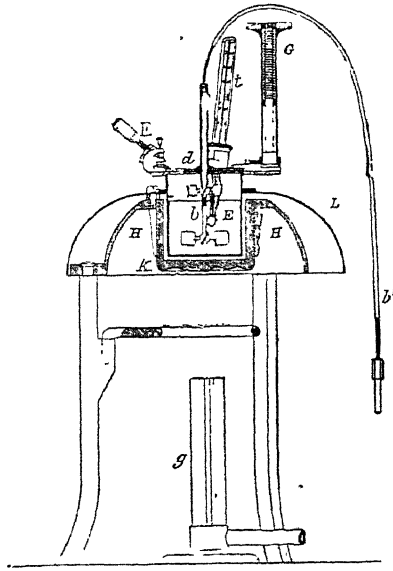


FIG. 100.

The *flash-point* is determined by the Pensky-Martens apparatus (Figs. 99 and 100), which is analogous to the Abel apparatus (p. 73) but without the water-bath, being furnished instead with a stirrer with vanes, b, moved by twisting the metal cord, b', between the fingers; it works similarly to the Abel apparatus, and the small flame, E, applied automatically, is fed by a small gas tube, H, and is relighted, every time it is extinguished, by another flame by its side. The thermometer, t, is graduated from 80° to 320°, and the heating is effected by the triple gas-burner, g, so that the temperature rises 5° per minute; observations are made by releasing the spring, at first for every 2° and later for every 1° rise of temperature.

The *acidity* is determined by titrating 50 c.c. of the 100 c.c. of 50 per cent. alcohol (neutralised) shaken up with 10 grms. of the mineral oil.

It is sometimes useful to know if certain more or less dark mineral oils are true refined products obtained by the distillation of petroleum residues (masut, &c.), or if they are merely the crude residues themselves diluted with more or less mineral oil. Charitschkoff (1907) found that the rise of temperature on mixing with concentrated sulphuric acid (Maumené number) in a Beckmann apparatus (*see* Molecular Weights, vol. i.) is 2·2–3·5° for all distilled products (solar oil and various lubricating oils) and 4–8·5° for all non-distilled products (crude naphtha, masut, &c.).

(*B*) VASELINE (or *mineral fat*). This was prepared for the first time by Cheeseborough in 1871 and forms a white, buttery mass constituted almost exclusively of various high, saturated hydrocarbons.

It is prepared, especially in America, by heating certain pale, crude, Pennsylvanian petroleums by direct fire in open boilers, and passing into the mass a current of hot air until the desired consistency or specific gravity (0·86–0·87) is reached. The mass is then decolorised by passing it, while still hot, repeatedly through animal charcoal or other decolorising agents (*see* p. 77). It is also prepared from the residues of Galician and German petroleum by diluting them with benzine and repeatedly refining with concentrated sulphuric acid. It melts at 33–40°.

Artificial vaselines are also placed on the market, these being obtained by dissolving paraffin or cerasin (*see later*) in paraffin oil; they can be distinguished from the natural vaselines, the latter being sticky and ropy and the former not. At 60° the viscosity (Engler) of the natural vaselines is 4·5–7·5, and that of the artificial ones little more than 1; the latter contain 11–35 per cent. and the natural vaselines 63–80 per cent. of paraffin, insoluble in 98 per cent. alcohol at 0°. The natural vaseline after solution in ether and precipitation with alcohol forms a sticky mass and the liquid remains turbid; the artificial variety, on the other hand, is precipitated in flocks and the liquid is left clear.

Gelatinised oil of vaseline, also prepared nowadays, is transparent and does not deposit paraffin, even if added in considerable quantity; it is obtained by heating vaseline oil (sometimes with a little sulphuric acid) at about 200° and adding, at a certain moment, a small quantity of soap.

For the decolorisation of vaseline and oil of vaseline *see above*.

Vaseline is used in pharmacy for the preparation of unguent medicines, also for the preparation of lubricants, and, in large quantities, for coating metallic articles to preserve them from rusting and oxidation; it is also used in the manufacture of smokeless powder.

(*C*) PARAFFIN. This was first found in petroleum by Fuchs in 1809 and Reichenbach obtained it from wood-tar in 1830, and showed its great importance as an illuminant.

It was obtained later by distilling lignites and bituminous schists. To-day it is largely prepared also from the denser American mineral oils (0·8588 and upwards), which on cooling deposit scales of paraffin.

For this purpose an apparatus consisting of three vertical concentric cylinders is used; in the inner and outer ones circulates a non-solidifying freezing solution, which has a temperature of −20° and serves to separate the paraffin from the mineral oil in the middle cylinder. According to J. Weiser (Ger. Pat. 226,136 and 227,334), paraffin is obtained from petroleum and tar residues by dissolving them in hot benzine and glacial acetic acid; on cooling, the solutions deposit paraffin, cerasin, or ozokerite. To free the flakes of paraffin from the adhering oil the cold mass is pressed in filter-presses (up to 15 atmos.) and the cakes thus formed are finally squeezed in hydraulic presses, as is done in the case of stearine (*see this*); the blocks of paraffin are then spread out in a warm chamber, where the last traces of coloured oils flow away. In the Weiser process the hydraulic presses are replaced advantageously by filtering tubes wound round with linen; the paraffin from the filter-press is broken up and forced into these tubes, being afterwards removed by steam and sent to the sweating chamber.

Hard paraffin melts at 54–60°, has sp. gr. 0·898–0·915, and forms a white, translucent mass used for the manufacture of paraffin candles; it is soluble in ether or benzene, insoluble in alcohol, acetic acid, and acetone. *Soft paraffin* with m.pt. 42–48° and sp. gr. 0·88–0·89 is used as an adjunct in wax and stearine candles, to impregnate wooden matches, in dressing textiles and as a preventive of frothing during the concentration of saccharine juices (*see* Sugar); it serves also as an insulator of electrical conductors and as a cold bath in the manufacture of *hardened glass*.

Most of the *paraffin* and *paraffin oil* is obtained from *ozokerite* (*see later*), the tar distilled from the lignites of Saxony and Thuringia (pyropissite) and from the bituminous shales of Scotland and Australia, and also from boghead coal.

I. PYROPISSITE is a special and interesting lignite now almost exhausted, is obtained from deposits of oily wood, and is extracted from the mines in Saxony and Thuringia in moist (up to 55 per cent. water) more or less plastic masses which feel greasy and when dry become friable and readily burn ; it has a dark yellow or brown colour. In the dry state it gives up to alcohol 20 per cent. of its weight of a substance, m.pt. 75–86°, giving paraffin oil on distillation. The composition of a good air-dried pyropissite was found to be: water, 33 per cent. ; ash, 6·51 ; C, 43·81 ; H, 6·97 ; N, 0·003 ; O, 8·81. When distilled in glass retorts in the laboratory it gives about 66 per cent. of tar, 26 per cent. of coke, and 8 per cent. of gas ; sometimes as much as 73 per cent. of tar is obtained. The industrial distillation of these lignites is carried out in large vertical refractory retorts, 8 metres high and 2 metres wide, placed in a suitable furnace so that the external walls are heated by rational circulation of the hot gases. Inside the retort are arranged numbers of iron capsules, inverted one on the other with a certain distance between, and a diameter 12–20 cm. less than that of the retort. The lignite is charged in lumps at the top and descends gradually in the free annular space between the walls of the retort and the edges of the capsule. When it reaches the bottom it consists of nothing but coke, which is occasionally discharged, fresh lignite being introduced at the top ; the gaseous products are evolved by a large tube at the top, and the tarry products (tar) flow down the walls of the capsules and are collected by a lower tube. The retorts are maintained at a dull red heat.

Lignite tar is brownish yellow to black in colour, has a peculiar odour, and liquefies between 15° and 30°, giving a greenish fluorescence. Its specific gravity is 0·820–0·935, or usually 0·840 at 35°. It has an alkaline reaction (from ammonia, ethylamine, &c.) and contains about 20–25 per cent. of paraffin. The best lignites give the less dense tars. According to the nature of the tar, the paraffin [1] is obtained from it in the following ways (*see also* Part III, Distillation of Tar):

(1) With very dense tars, in order to separate the creosote and certain resinous substances more efficiently, vacuum distillation in large direct-fired boilers is resorted to. This yields 25–50 per cent. of fatty oils, 50–65 per cent. of crude paraffin, and 7–9 per cent. of coke, which is burnt, together with the gases from the distillation, to heat the boilers. The mass of crude paraffin is purified with acid and alkali, or with acid and subsequent distillation. The more solid part is then separated from the oily part by cooling the mass in vessels holding 100–200 kilos, around which circulates a very cold solution (the non-solidifying liquids used for ice-machines, *see* vol. i, p. 231). When the oily or buttery part (which is distilled for the extraction of solar oil and second-grade paraffin) is separated by filtration from the crystallised paraffin, the cakes of the latter are pressed in hydraulic presses at 150 atmos. to remove the 20 per cent. of oil still contained in them. The solid cakes which remain are yellowish in colour, and are purified by melting them several times with 10–15 per cent. of benzine and pressing them at 200 atmos. in a hydraulic press. To get rid of the smell of benzine the paraffin is heated in iron cylinders with high-pressure steam, the hot paraffin being then passed through the decolorising material (animal charcoal, ferrocyanide residues, or magnesium hydrosilicate clay (*see* p. 77)). The small quantity of this material retained by the paraffin is finally removed by

[1] Now that the deposits of *pyropissite* are almost exhausted and the paraffin industry of Saxony and Thuringia has been subjected to the competition, first, of ozokerite (after 1870), and then (after 1880) to the more serious one of the American paraffin extracted from Ohio petroleums—which has invaded all the markets of the world—it has been recently discovered that when pyropissite is distilled a great part of the paraffin is destroyed, much better yields being obtained by extracting direct with suitable solvents, which, after evaporation, leave a waxy mass ; when this is purified with fuming sulphuric acid, it yields an almost white product of great value—the *montan wax* (Bergwachs), similar to *cerasin* (mineral wax). The remedy for the paraffin crisis of Saxony and Thuringia has arrived too late, since the valuable paraffin has been squandered by distillation. Other layers of lignite are being worked to-day, and these are extracted in the hot with benzine ; the solution of bitumen extracted is first purified by thorough cooling, the paraffins being thus separated while the resins (these are recovered by evaporation of the solvent ; they melt at 50° to 60° and form 15 to 25 per cent. of the crude bitumen) remain in solution. The bitumen separated in the cold is redissolved in benzine and treated with concentrated sulphuric acid, the mass being kept mixed and slowly heated to boiling. Animal charcoal is added and the liquid filtered, passed over fuller's-earth (*see* p. 77), and neutralised by passing in a little gaseous ammonia. After distillation of the solvent there remains a yellowish or almost white paraffin melting at 82° to 85° (Ger. Pat. 216,281, 1907)

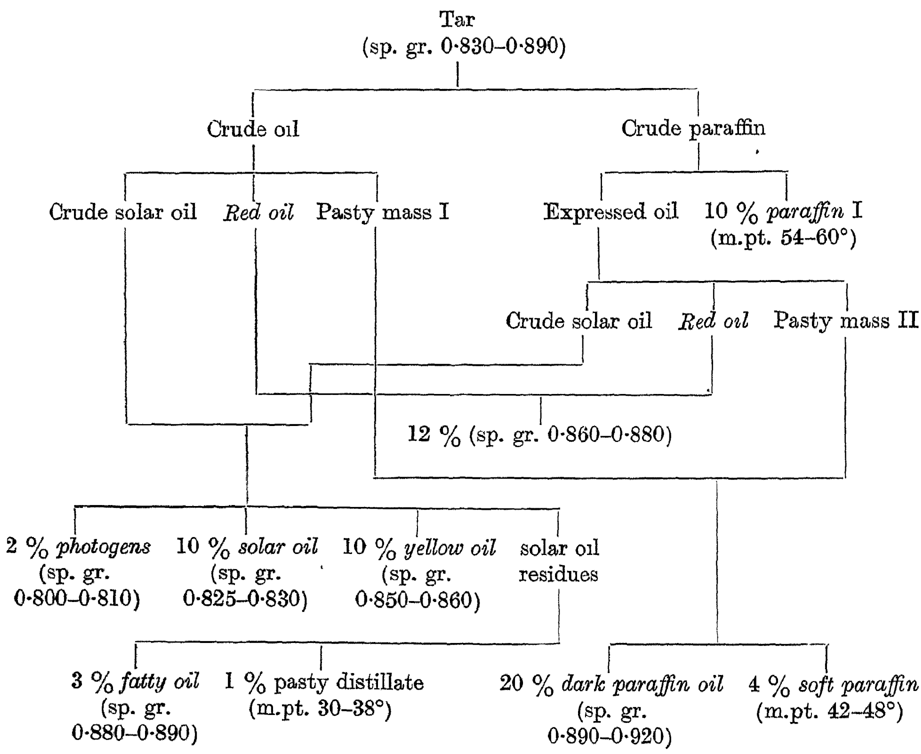
filtration through paper, the paraffin being then allowed to solidify in large shallow moulds.

Miss Az has recently suggested the purification of crude paraffin by treating it either fused or as powder, between 60° and 70°, with a solvent (methyl or ethyl alcohol, acetone, or acetic acid or anhydride). The paraffin is insoluble and the impurities soluble in these solvents. Paraffin thus purified appears to be of better quality than that purified in the ordinary way.

The tar is sometimes distilled with superheated steam ; in other cases only the benzines (*photogens*) and the light oils are distilled, the residue being cooled to a low temperature and the solid paraffin which separates centrifugated to eliminate the tar and heavy oils. When the tars are very dense (above 0·900) Krey finds it convenient to distil them under a pressure of about 10 atmos., thus raising the temperature to 400–450°. This yields 60 per cent. of distilled oil of sp. gr. 0·830, which is largely used for the preparation of oil-gas (*see* p. 57), 10 per cent. of gas, and 30 per cent. of residual oily tar.

(2) With light and very pure tars a greater yield of paraffin is obtained more cheaply by treating the tar directly with concentrated sulphuric acid, washing with water, and subjecting to fractional distillation over calcium hydroxide. Crystallisation, pressing, and bleaching are carried out as described above.

The following scheme shows the different operations and the final yields in a tar distillation (the brackets unite products which are worked up together, generally by distillation ; the ultimate products are shown in italics) :



Photogen is a species of benzine similar to that of petroleum, but obtained by the distillation of wood, lignite, and coal ; it is used in the purification of paraffin, in the carburetting of lighting gas, and for removing spots from fabrics. *Yellow oil* is used for the extraction of fats and for cleaning ; *red oil* (sp. gr. 0·860–0·880) has various uses, and serves well for the manufacture of oil-gas (*see* p. 57) ; the fatty oils and dark paraffin oils (0·880–0·925) are used as *oil for gas* and for making *cart-grease*[1] ; the yellow and red oils (0·880–0·900) are used as thinner lubricants.

[1] **Oils for Gas.** From the time when gasworks began to mix gas obtained by the carbonisation of bituminous coal with carburetted *water-gas* and with *oil-gas* (in 1905 Germany produced 30,000,000 cu. metres, England

The washing of tar and of its distillates with alkali removes the *creosote* which is liberated by sulphuric or carbonic acid (*see* Part III). Washing with acid separates resinous masses which are set free by diluting the acid mass with water, this removing the acid. Distillation of these resinous masses with varying proportions of creosote oil and at different temperatures yields *goudron* or *asphalte tar*, or *artificial bitumen*,[1] which is used in the manufacture of *impermeable pasteboard* for roofing, in rendering woodwork and masonry (especially in damp houses) damp-proof, and also in the manufacture of ultramarine.

II. Another important source of paraffin is furnished by the **Bituminous Schists**, which are especially abundant in the Lothians in Scotland. In 1848 Young and Meldrum began to work and purify a special oil issuing from the surface of the soil in

500,000,000 cu metres, and the United States 1,550,000,000 cu metres of carburetted water-gas), the use of mineral oils for carburetting the water-gas and for producing oil-gas has increased considerably. These oils for gasifying are obtained partly by the distillation of lignite and shale tars (*see* pp. 116, 119), but more especially by the distillation of petroleum residues (*solar oil*, intermediate to true petroleum and lubricating oils). The price of these oils increases with the narrowness of the temperature limits within which they boil; these limits are usually 100° apart and it is of no consequence whether they be 200° and 300° or 250° and 350°; they should contain less than 25 per cent of unsaturated hydrocarbons (soluble in concentrated sulphuric acid of sp. gr. 1 83), otherwise they give too much tar and coke on gasification; they should contain not more than 30 per cent of creosote, but a high proportion of paraffin is advantageous. In the United States 600,000 tons are consumed annually; about 220,000 tons (in 1906) are imported into England, and about 4153 tons of mineral oils (sp gr. 0·83–0 83) into Germany for the carburetting of water-gas; but Germany itself produces a further quantity of about 300,000 tons of oil for gasifying, 13,000 tons being used for producing oil-gas on the railways, and 9000 tons for mineral-oil engines. For the carburetting of gas these oils should cost less than 9*s*. 6*d* per quintal.

[1] Asphlate, Pitch, and Bitumen. When *tar from the distillation of wood* (or lignite) is heated until all the volatile products are eliminated, there remains a black mass which, when cold, assumes a glassy consistency and forms *pitch*, used particularly for caulking ships, for preparing shoemakers' thread, and for making cements impermeable to water, &c

When *coal-tar* is completely distilled it leaves a more or less hard black residue—*coal-pitch*—which is used for ordinary asphalting and for making varnishes, lacs, and coal briquettes (*see* vol. i, p. 369). Pitch is also prepared expressly by prolonged heating of tar in a current of air or with sulphuric acid.

Bitumen (*mineral pitch*) bears sometimes the unsuitable name, *natural asphalte*, and forms a fragile, blackish brown mass, which, on heating, softens between 100° and 135°; it has the sp. gr. 1·10–1·20 and the hardness 2. It burns readily with a very smoky flame, is insoluble in water, alkali or acid, slightly soluble in alcohol or ether and readily soluble in benzene, carbon disulphide and turpentine (in which it ceases to be soluble after exposure to light, and is hence used in photo-lithography). The best bitumen is found at the surface of the Dead Sea in Palestine, and in greater quantities at the *Pitch Lake* in the island of Trinidad; it abounds also in Syria, Utah, Venezuela, and Cuba, and at Dax (France). That of Trinidad is the best and contains 40 to 50 per cent. of pure bitumen and 30 per cent of mineral substances, the remainder consisting of organic substances and water. It is roughly refined on the spot by melting at 160–170° in open vessels to separate part of the mineral substances, the product thus obtained containing 56 to 58 per cent. of pure bitumen, having the sp. gr. 1·40–1·43 and softening at 85°–95°, the portion soluble in petroleum ether bears the name *petrolene*. The amount of change, or efflorescence, which bitumen will undergo under the action of air and light can be estimated by determining the proportions of *carbenes* present, *i.e.* the products insoluble in carbon tetrachloride but soluble in carbon disulphide.

Pure bitumen is used for making black sealing-wax, black lacs and varnishes, and also lamp-black; the lower qualities serve for coating wooden structures (boats, telegraph poles), for cardboard, for roofs, and damp walls, &c.

In order to distinguish natural from *artificial bitumen*, about 1 grm. of the substance is heated to 200°, cooled, powdered, and treated with 5 c.c. of 80 per cent. alcohol; if the latter turns yellow and exhibits fluorescence, artificial bitumen is indicated, whilst if the alcohol remains almost colourless, the bitumen is natural.

By the term *asphalte* (natural) is meant minerals, rocks, and earth containing bitumen; gravelly stones impregnated with bitumen, as has been mentioned above, are treated for the extraction of refined bitumen by heating with water, whilst calcareous bituminous stones containing 5 to 14 per cent. (sometimes 20 per cent) of pure bitumen, are used for the preparation of *asphalte mastic* by powdering and fusing them homogeneously with a certain quantity of bitumen. This mastic is cooled in moulds and is used directly for paving streets and terraces, either alone or mixed with fine sand or gravel Powdered asphalte can also be used for paving, by spreading it out and compressing it with heavy cast-iron double rollers heated inside.

In California, large quantities of *artificial asphalte* are prepared by prolonged injection of air into dark mineral oils (sp. gr. 0·9333 to 0·9859) heated at 650°. Fusion of colophony at 250° and addition of sulphur yields an asphalte which is similar to that of Syria and is used in photography.

Natural asphalte occurs abundantly near Neuchâtel, in the Department of Ain (France), in the neighbourhood of Hanover, and at Lettomonapello in Italy (the product of this locality is worked at S. Valentino, near Chieti).

Statistics and Prices. *Pitch:* Italy produced 4820 tons of the value £9600 in 1909; England exported 30,000 tons in 1909 and 36,000 tons in 1910, and imported 8000 tons in 1909 and 12,200 tons in 1910; Germany imported 39,251 and exported 22,387 tons in 1908, and imported 28,434 and exported 34,816 tons in 1909.

Asphalte: In 1909 Italy produced 111,067 tons of asphaltic rock, 26,588 tons of pulverised asphaltic rock, 8250 tons of artificial asphalte (obtained by mixing the coke remaining from the distillation of tar with sand &c.) and 731 tons of compressed asphalte bricks. This production takes place mainly in Central Italy and in Sicily (at Ragusa di Siracusa and Modica; the asphalte rocks of the latter locality, according to A. Coppadoro (1910) contain 7 to 14 per cent. of bitumen and 82 to 89 per cent. of calcium carbonate). In 1909 Italy exported a total of 21,978 tons (of the value £132,000) of these substances under the name *solid bitumen* (27,175 tons in 1906; 26,036 tons in 1907; 24,158 tons in 1908). In 1908 Germany imported 130,062 tons (98,370 tons in 1909) and exported 13,280 tons (14,200 in 1909); it produced 103,000 tons in 1905; 89,000 tons in 1908 (value £40,000), and 77,500 tons in 1909. Trinidad exported asphalte to the value of £115,800 in 1905 and £133,200 in 1906.

The price of tar is 6*s*. 7*d*. per quintal: Archangel pitch I, 22*s*. 5*d*.; Swedish pitch, 18*s*. 5*d*.; coal pitch, 4*s*. to 4*s*. 10*d*.; lignite pitch, 4*s*. 10*d*. to 6*s*. 5*d*.; stearine pitch, 14*s*. 5*d*. to 28*s*. 10*d*.; Syrian asphalte I, 68*s*.; asphalte in fine powder, 140*s*.

Derbyshire, and, having exhausted this deposit and not finding others, they succeeded in preparing mineral oils, which had been already introduced for illuminating purposes, by distilling cannel coal, which gave much lower but remunerative yields.

In about 1860 they discovered that the interesting Scotch deposits of boghead coal gave a yield of oil much greater than cannel coal, and in 1864 and 1866 were erected the two works at Bathgater and Addiwell, which became world famous. The deposits of boghead coal were exhausted in four or five years, and were then replaced by the more abundant although less fertile deposits of *bituminous schists* (*shales*) in which Scotland is so rich. The invasion of American petroleum in about 1880 created a serious crisis in this industry, which was partially saved by new and improved technical methods introduced by engineers and chemists, especially by Henderson ; the by-products were more completely utilised, the furnaces improved, fractional distillation apparatus brought into use, the ammoniacal liquors utilised, the tar, coke, gas, and final residues employed as fuel and the labour reduced to a minimum ; the mineral oils came to occupy a secondary position, attention being paid to the production of paraffin and high-class lubricating oils for engines.

In France these bituminous schists, which abound in the basin of the Autun and at Buxière-les-Mines, were first worked in 1837 by Selligne in consequence of the studies of Reichenbach (1830), and the industry became a flourishing one about 1860 ; in 1864, 128,550 tons of shale were distilled, producing 4750 tons of crude oil, destined principally to prepare oil-gas in the large towns. The invasion of American petroleums also overthrew this industry, which is now only partially supported by the Customs duty.

A bituminous schist from Midlothian (Scotland) gave on analysis: 20 per cent. carbon, 0·7 per cent. nitrogen, 1·5 per cent. sulphur, the rest being mineral matter ; it gave up nothing soluble to ether.

The industrial distillation is carried out in batteries of vertical retorts arranged in a furnace and heated also internally with superheated steam. The products of distillation are condensed with apparatus similar to that used for illuminating gas, the residues from the retorts, containing as much as 12 per cent. of combustible substances, being burnt in the furnaces. The distillation lasts from 4 to 6 hours, or, for large retorts holding 2 tons, 24 hours. The yield consists of about 4 per cent. of gas, 8 per cent. of ammoniacal liquor (ammonium carbonate), 12 per cent. of crude oil, 76 per cent. of residue. The crude oil contains less than 0·03 per cent. of sulphur ; the gas evolved contains 21–23 per cent. CO_2 ; 1–4 per cent. CO ; 13–24 per cent. H ; 1·6 per cent. of heavy hydrocarbons ; 8–20 per cent. CH_4 ; 1·2–4 per cent. O ; and 35–43 per cent. N.

The crude oil is dark green and has a sp. gr. 0·865–0·885, and is semi-solid at ordinary temperatures owing to the paraffin present.

This oil is treated by virtually the same methods as are used for lignite tar, that is, by continuous distillation in a current of steam, so as to obtain purer products. The first distillation gives : *green naphtha* (0·753) and *green oil* (0·858), which are purified by acid and alkali and then redistilled: the first gives commercial mineral oil (also solar oil) and the second light oils and paraffin, which is separated by cooling from the *blue oil*, which serves as a good lubricant when refined. The paraffin is purified by the process given above (paraffin of lignite tar).

A ton of bituminous schist (of the value of 12*s*. 9½*d*.) yields about 8 kilos of naphtha, 115 kilos of crude oil (green oil), and 13 kilos of ammonium sulphate. From 100 kilos of green oil are then obtained 31 kilos of burning oil, 13 kilos of lighting oil, 11 kilos of midlle oil, 15 kilos of paraffin, and 15–20 per cent. of loss, the remainder being coke or tar.[1]

[1] Ichthyol is an oil obtained by the dry distillation of a bituminous shale occurring abundantly in the Tyrol (at Seefeld), and at Besano (Varese), and Melide (Switzerland). On distillation it yields, besides illuminating gas, 5 to 7 per cent of crude, utilisable ichthyol (for the Melide shales) containing 5 per cent. (Besano) or 10 per cent. (Seefeld) of combined sulphur and 6 to 7 per cent. of nitrogen. On distillation, these shales lose 30 to 40 per cent of their weight. The Besano oil is richer in pyridine bases than that of Seefeld, which contains 1 per cent. of them (Baumann and Schotten, Contardi, and Malerba).

Treatment of this oil with concentrated sulphuric acid yields *ichthyolsulphonic acid* containing 10 to 15 per cent. S (like sulphoricinates) and forming salts (*ichthyolsulphonates*) with soda or better with ammonia, which are used in the cure of skin diseases. *Ammonium ichthyolsulphonate* ($C_{22}H_{36}O_6S_3(NH_4)_2$?), which commonly bears the name of ichthyol, forms a dense, reddish brown liquid, soluble in water, and its solution gives a black resinous deposit with HCl and yields NH_3 when treated with KOH.

When distilled with steam (or treated with hydrogen peroxide) ichthyol loses its unpleasant odour, the deodorised product being termed *desichthyol*. Of the many other derivatives (and substitutes, *e.g. thyol*, obtained by treating tar oils with sulphur), mention may be made of *ichthyoform* (blackish brown, inodorous), prepared by

The oily schists of Australia (77 miles from Sydney) give, on distillation: 68 per cent. of oils, 14 per cent. of gas, 11 per cent. of crude paraffin wax, and 7 per cent. of ash.

In 1873, 524 tons of oily shales were treated in Scotland; in 1893 about 2,000,000 tons, and in 1909 3,000,000 tons, giving 280,000 tons of crude oil. The Scotch shale-oil refineries produced in 1908 90,000 tons of burning oil, 16,000 tons of engine oil, 40,000 tons of gas-oil, 40,000 tons of lubricating oil, 25,000 tons of paraffin wax, and 60,000 tons of ammonium sulphate. In 1908 134,163 tons of bituminous shale of the value £72,4C0 were produced in Italy. In France 219,000 cu. metres were distilled in 1890.

In Germany 80,000 tons of lignite tar (corresponding with 600,000 tons of lignite) are distilled annually, and the products obtained (9000 tons of paraffin wax—two-thirds hard and one-third soft—5000 tons of solar oil, and 3500 tons of heavy oil) have a value of about £880,000.

Tar can be purchased from the lignite distilleries at little more than 10*d.* per quintal, and, treated as above, yields 14*s.* 5*d.* to 16*s.*, taking as the average selling prices per quintal: paraffin wax, £3 12*s.*; solar oil, 10*s.* 5*d.*; yellow oil of paraffin, 12*s.* 10*d.*; dark oil of paraffin, 10*s.* 5*d.*, which are about 25 per cent. less than the market prices.

III. The third source, one of the most important, of *paraffin wax* is Ozokerite (or *mineral wax*). It is found in England, Russia, and America, but the deposits of greatest industrial and historical importance are those of Galicia (Boryslaw, Pomiarki, Starunia, &c.), where it occurs in seams as much as a metre in thickness. It was discovered by Doms when searching for petroleum, and from 1860 to 1870 was worked by the Landesberg process for the extraction of paraffin wax, which competed keenly with that of Saxony and Thuringia (from lignite); in 1870, Pilt and Ujhelyi found that simple treatment of ozokerite with concentrated sulphuric acid, followed by decolorisation with animal black, yields *cerasin*, a product of greater value than, and similar to, beeswax.[1] In the State of Utah, the industrial treatment of ozokerite was begun in 1888, and in 1890 already yielded as much as 600 tons of crude cerasin.

Ozokerite forms an amorphous mass of a yellow, brown, greenish, or black colour and of varying consistency; the harder varieties show a fibrous fracture; the specific gravity is 0·85–0·95, and the m.pt. 55–110° (usually between 60° and 79°); it contains 85 to 86 per cent. of carbon and 14 to 15 per cent. of hydrogen, and hence consists principally of paraffins, together with a small proportion of olefines; it is soluble in benzine, turpentine, petroleum, ether, and carbon disulphide, but only slightly so in alcohol. It forms an excellent electrical insulator and can be used in place of gutta-percha.

According to Höfer, ozokerite has been formed by the slow evaporation, during many centuries, of petroleum rich in paraffin.

On distillation, it yields: 2 to 8 per cent. of benzine, 15 to 20 per cent. of naphtha, 36 to 50 per cent. of paraffin wax, 15 to 20 per cent. of heavy oils, and 10 to 20 per cent. of residual solids.

STATISTICS AND PRICE OF PARAFFIN WAX. In 1908 fourteen factories in Germany treated 70,000 tons of lignite tar, worth about £160,000, and produced 45,000

treating ichthyolsulphonic acid with formaldehyde and used as an antiseptic for the intestines and instead of iodoform for curing wounds: it costs £4 per kilo and ammonium ichthyolsulphonate £1 per kilo.

[1] The material from the mines (shafts 80 metres or more in depth), which contains admixed earth and stones, is placed in open vessels holding 300 litres and heated by direct fire heat; the mineral matter settles to the bottom and is separated by decantation. This matter still contains 10 per cent. of wax, which is extracted with benzine; both this and the decanted part form the prime materials treated in the refineries found in all countries.

The refining is carried out in large iron boilers holding up to 3000 kilos of the crude wax, half a metre being left free to take the scum which forms. The fused mass is kept at 115–120° for four to five hours and is stirred to liberate all the water; 15 to 25 per cent. (according to the quality of the wax) of fuming sulphuric acid containing 78 per cent. of SO_3 is then added, in a thin stream, to the mass, which is thoroughly stirred meanwhile; the temperature rises slowly to 165° and then to 175°, the oxidisable impurities separating as a black mass (asphalte) and the excess of sulphuric acid evaporating. The vessel is covered and provided with a draught-pipe to carry off the acid vapours. The mass is allowed to cool slowly, being neutralised with residues from the manufacture of ferrocyanide, decolorised with animal black and sent to the filter-presses. The mass obtained is still slightly yellow and is whitened by further treatment with sulphuric acid. When beeswax is to be imitated, quinoline yellow or other coal-tar dye is added.

tons of oil, 11,000 tons of crude paraffin wax (equal to 7600 tons of the pure wax, worth £220,000), and 8000 tons of creosote, tar and pitch, of the total value of £450,000 ; about 1,000,000 tons of lignite were distilled and 350,000 tons of coke left. For several years, however, the industry has been stationary. The market price of paraffin wax varies somewhat with its melting-point[1] ; white, m.pt. 38–40°, costs 78*s*. per quintal ; that melting at 42–44°, 82*s*. 6*d*. ; at 48–50°, 85*s*. 6*d*. ; at 56–58°, 92*s*. ; and at 60–62°, £5. That used in pharmacy, m.pt. 74–76°, costs as much as £9 12*s*. Crude paraffin wax is sold for about 56*s*. During recent years, however, the price has diminished considerably owing to the great production in Galicia (54,000 tons in 1909 and 62,000 in 1910), whence a considerable quantity is exported into Germany even at less than 32*s*. per quintal.

In 1909 England imported 53,000 tons (£1,126,000) of paraffin, and exported 17,400 tons (£407,024) ; in 1910 the exports were valued at £288,457.

In 1903 Italy imported 9526 tons of solid paraffin ; in 1905 about 8880 tons ; in 1909 17,400 tons, and in 1910 19,153 tons of the value of £400,000, in addition to 108 tons of *cerasin* worth £4340. The production of paraffin in the United States has become of great importance, the Standard Oil Company having almost the monopoly (95 per cent. of the American output) ; the exportation was 75,000 tons in 1905, 85,000 tons in 1909, 95,000 tons (£1,465,800) in 1910, and 97,000 tons (£1,409,600) in 1911. From the bituminous shales of Scotland 23,000 tons of paraffin wax were obtained in 1910.

Pure white *cerasin* resembles wax, melts at 62–80°, and has the sp. gr. 0·918–0·922. It is used in making candles, in perfumery, and as dressing for textiles. It is subject to much adulteration owing to its high price ; the yellow of the first quality, m.pt. 62–63°, costs 108*s*. or more per quintal ; the second quality 92*s*. ; that melting at 68–70° costs £6, and the white, m.pt. 62–63°, £6 12*s*.[2]

The *ozokerite* worked in Austria-Hungary in 1877 amounted to 8961 tons ; in 1885, 13,000 tons ; and in 1894, 6742 tons. The exportation of cerasin was 3594 tons in 1891 and 2382 tons in 1895.

In the United States the production of refined ozokerite, which was 160 tons in 1888 rose in 1892 to 75,000 tons, of the value of £4,000,000.

[1] The estimation of the paraffin wax in a commercial sample of *hard paraffin* is made by Holde's method : 1 grm. is dissolved in a test-tube in ether—excess of which is avoided—the solution cooled to − 20° or − 21° and an equal quantity of absolute alcohol added ; the paraffin is thus separated in flakes, and if the mass is too hard to be filtered, it is diluted with the mixture of alcohol and ether cooled to − 20° (*see* Freezing Mixtures, vol. i, p. 229). The filtration is effected under pressure in a funnel surrounded with the freezing mixture, the paraffin being washed with the alcohol-ether mixture and the washings kept separate from the first filtrate ; the latter is freed from the solvent by evaporation, and any paraffin wax that may have been dissolved then estimated. The paraffin on the filter is dissolved in hot benzine, the solution evaporated in a tared dish, and the residue dried at 105° and weighed ; the percentage of paraffin wax found is increased by 1 to correct for constant errors of analysis. The apparatus used is shown in Fig. 101 ; the solution to be filtered is kept cold in the test-tubes immersed in the freezing mixture, 3, surrounded by felt, 2 ; the water from the freezing mixture runs off at 5 and that which drops collects in 4.

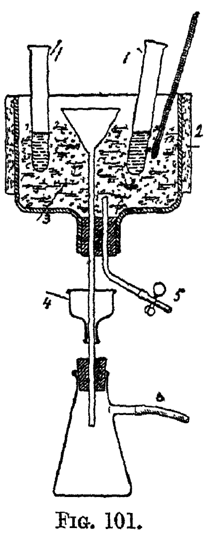


Fig. 101.

With *soft paraffin* wax Eisenlohr's method is used : 0·5 grm. of the substance is dissolved in 100 c.c. of absolute alcohol, 25 c.c of water being added and the solution cooled to − 18° or − 20°. The separated paraffin is filtered as described above and washed with 80 per cent. (by volume) alcohol until the filtrate no longer turns turbid on addition of water. It is dried *in vacuo* at 40° until constant.

To detect the addition of even small quantities of *cerasin* (*see above*) Graefe dissolves 1 grm. in 10 c.c of carbon disulphide at 20° and treats 1 c.c. of this solution with 10 c.c. of a mixture of equal volumes of alcohol and ether. If undissolved flocks remain even after heating and subsequent cooling, the presence of cerasin is certain ; this result can be confirmed by means of the Zeiss oleo-refractometer, paraffin wax at 90° showing 1·5 to 4, and cerasin 11·5 to 13 (Ulzer and Sommer, 1906 ; Berlinerblau, 1903).

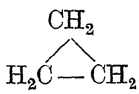
A *mixture of cerasin and paraffin wax* can be detected by the following test : a glass rod 3 mm. in diameter in diameter is immersed to a depth of 1 cm. in the fused substance, extracted, allowed to cool and hung in a test-tube heated externally with water. If the wax drops above 66°, it is pure cerasin, whereas if it drops below 66° it is regarded as mixed with paraffin wax or as the latter alone. The dropping-point can also be determined with the Ubbelohde apparatus (p. 6). Addition of colophony is recognised by the *acid number* or saponification number, colophony being saponifiable and cerasin not.

(b) UNSATURATED HYDROCARBONS

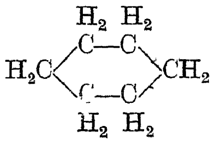
I. ETHYLENE SERIES: C_nH_{2n} (Alkylenes or Olefines)

Two groups belong to this series, the *olefine* group, the first member of which is ethylene, C_2H_4, the succeeding ones being open-chain hydrocarbons with a double linking between two carbon atoms, since hydrogen, halogens, ozone, &c., can be readily added to them, transforming them into saturated compounds of the paraffin series.

The other group yields additive products only with difficulty, and its members are formed of closed carbon-chains (*cyclic compounds*). The first term is *trimethylene* or *cyclopropane*, *hexamethylene*, and higher compounds being known:



Trimethylene



Hexamethylene

The carbon atoms in these last compounds are all in the same conditions and cannot be differentiated. The cyclic compounds will be studied in a separate section of the aromatic series (Part III).

The following Table gives the more important members of the olefine series (the number in parentheses representing boiling-points under reduced pressure):

	Melting-point	Boiling-point		Melting-point	Boiling-point
Ethylene, C_2H_4	−169°	−103°	Decylene, $C_{10}H_{20}$	—	172°
Propylene, C_3H_6	—	−48°	Endecylene, $C_{11}H_{22}$	—	195°
Butylene (3 isoms.), C_4H_8 α	—	−5°	Dodecylene, $C_{12}H_{24}$	−31°	(96°)
β	—	+1°	Tridecylene, $C_{13}H_{28}$	—	233°
γ	—	−6°	Tetradecylene, $C_{14}H_{28}$	−12°	(127°)
Amylene (5 isoms.),			Pentadecylene, $C_{15}H_{30}$	—	247°
C_5H_{10}; normal-amylene	—	+35°	Hexadecylene $C_{16}H_{32}$ (Cetene)	4°	274° (155°)
Hexylene, C_6H_{12}	—	68°	Octadecylene, $C_{18}H_{36}$	+18°	(179°)
Heptylene, C_7H_{14}	—	98°	Eicosylene, $C_{20}H_{40}$	—	—
Octylene, C_8H_{16}	—	124°	Cerolene, $C_{27}H_{54}$	+58°	—
Nonylene, C_9H_{18}	—	153°	Melene, $C_{30}H_{60}$	+62°	—

The *official nomenclature* of the olefines is the same as that of the paraffins, excepting that the final *ane* is changed into *ene* (thus ethylene, which is isologous with ethane, is called *ethene*, and so on; *see also* p. 28).

These unsaturated hydrocarbons differ little in their *physical properties* from the corresponding saturated homologues.

The first terms—up to C_4H_8—are gases, and after C_5H_{10} come liquids with increasing boiling-points, these gradually approaching one another as in the paraffins; the higher members are solid and, like the paraffins, have a sp. gr. 0·63–0·79, are insoluble in water, but soluble in alcohol or ether.

The chemical properties differ somewhat from those of the saturated compounds. Thus, they readily take up HCl, HBr, HI, Cl, Br, I, fuming H_2SO_4, hypochlorous acid (giving chloro-alcohols or *chlorhydrins*, *e.g.*

$CH_2 : CH_2 + HClO = CH_2Cl \cdot CH_2OH$), hyponitrous acid, ozone, &c., forming compounds of the saturated series.

Cl is added more easily than I, Br occupying an intermediate position, whilst HI is added more easily than HBr, and this more easily than HCl. With these acids, the halogen is added to the carbon atom with which the least hydrogen is combined.

Ethylene unites with fuming sulphuric acid at the ordinary temperature and with the ordinary acid at 165°, forming ethylsulphuric acid, $C_2H_5O \cdot SO_3H$; with higher compounds, the acid radicle passes to the less hydrogenated carbon atom.

They often *polymerise* under the action of sulphuric acid or zinc chloride; for example, amylene, C_5H_{10} forms $C_{10}H_{20}$, and $C_{15}H_{30}$ gives $C_{20}H_{40}$.

They are readily *oxidisable*, for example, with potassium permanganate or chromic acid (not with nitric acid in the cold), the chain being then broken at the double linking, with formation of oxygenated compounds (acids) containing less numbers of carbon atoms in the molecule. Careful use of permanganate results initially in the addition of two hydroxyl groups without breaking the chain and forming dihydric alcohols (*glycols*), for example,

$$\begin{array}{c} OH \cdot CH - CH \cdot OH. \\ \;\;\;\;\;| \qquad\;\; | \end{array}$$[1]

Almost all compounds with a double linking between atoms of carbon give *Baeyer's reaction*, that is they rapidly discharge the violet colour of a dilute solution of potassium permanganate and sodium carbonate, with formation of a reddish brown flocculent precipitate of hydrated manganese peroxide.

This reaction is not given by reducing substances like aldehydes or by certain aromatic compounds (*phenanthrene*, &c.).

All compounds with doubly linked carbon atoms give the *ozone reaction* (Harries, 1905, and Molinari, 1907), that is, when dissolved in a suitable solvent they fix, *quantitatively* and in the cold, the ozone contained in a current of ozonised air passed through the solution; in this property they differ from compounds with either a triple linking or a benzene double linking (E. Molinari, *Ann. Soc. Chim.*, Milan, 1907, 116).

METHODS OF PREPARATION. (1) They are formed, together with petroleum, in the dry distillation of wood, lignite, coal, paraffin ("cracking," &c.).

(2) By eliminating water from the alcohols, $C_nH_{2n+1}OH$, by heating them with dehydrating agents (H_2SO_4, P_2O_5, $ZnCl_2$, &c.); a stable intermediate product is sometimes formed, *e.g.* ethyl-sulphuric acid, $C_2H_5 \cdot HSO_4$, which at a higher temperature gives ethylene and sulphuric acid. Higher alcohols and ethers are resolved, merely on heating, into olefines and water.

(3) From saturated halogen derivatives $C_nH_{2n+1}X$ (X = halogen), especially from secondary and tertiary bromo- and iodo-derivatives, by heating them with alcoholic potash, or by passing their vapours over heated lime or lead oxide, &c.

$$C_5H_{11}I + C_2H_5OK = KI + C_2H_5 \cdot OH + C_5H_{10}.$$

The mixed ether, $C_5H_{11} \cdot O \cdot C_2H_5$, may also be formed to some extent.

[1] From what has been said up to the present, it is obvious that a *double linking* does not signify a firmer union between carbon atoms; it is simply a convention. And the breaking of the chain, by oxidising agents, at the double linking is to be attributed to the ease of formation of intermediate products (*e.g.* dihydric alcohols) rather than to a less attraction existing between carbon and carbon at that point. Such readiness to react may, according to Baeyer, be explained by regarding the affinities of the carbon atom as orientated or grouped at four poles arranged like the vertices of a regular tetrahedron (*see* p. 18 *et seq.*). If two carbon atoms unite by a double linking the poles at the surface of the carbon atoms become displaced and approach one another, so that there results a certain *tension* which tends to restore the poles to their original positions (*Baeyer's tension hypothesis of valency*), and which explains the readiness with which the double linking reacts or opens. After the initial oxidation leading to these intermediate products, further action of the oxidising agent, as a general rule, *oxidises or breaks the chain at a point where oxygen already exists, that is where the oxidation is already begun* (*see* Part III, The Hypothesis of the Partial Valencies of the Benzene Nucleus).

(4) From dihalogenated compounds by heating with zinc :

$$C_2H_4Br_2 + Zn = ZnBr_2 + C_2H_4.$$

(5) By electrolysis of dibasic acids of the succinic acid series :

$$C_2H_4(COOH)_2 = C_2H_4 + 2CO_2 + H_2.$$

(6) Unsaturated compounds are obtained by heating the condensation products of the *ketenes* (*q.v.*).

CONSTITUTION OF THE OLEFINES. In this group it is assumed that between two carbon atoms there exists a double linking : $H_2C{=}CH_2$, $H_2C{=}CH{-}CH_3$, &c., the presence of two free valencies, thus, $H_2C{-}CH_2$ or $HC{-}CH_2$, being excluded for the following reasons :

In unsaturated compounds the addition of halogen does not take place at a single carbon atom, so that ethylene chloride, $C_2H_4Cl_2$, has not the formula $CH_3{\cdot}CHCl_2$, which is that of ethylidene chloride obtained from acetaldehyde, $CH_3{\cdot}CHO$, by replacement of the O by Cl_2 (by the action of PCl_5). Since ethylene chloride is chemically and physically different from ethylidene chloride, the former must have the constitutional formula, $CH_2Cl{-}CH_2Cl$, and the third formula for ethylene, $CH_3{-}CH{<}$ is thus excluded. The second formula is not probable because, if the existence of free valencies is assumed, they could also occur in non-adjacent carbon atoms, and thus give rise, in the higher hydrocarbons, to numerous isomerides which have, however, never been prepared (if propylene had two free valencies, four isomerides should exist, instead of only one) ; further, the addition of halogen always takes place at two contiguous carbon atoms (*see* Note on preceding page).

Finally, the admission of free valencies in organic compounds is inadmissible in view of the unsuccessful attempts to prepare *methylene* (or *methene*), CH_2, for instance, by eliminating HCl from methyl chloride, $2CH_3Cl = 2HCl + 2CH_2{<}$; the two methylene residues always condense, forming ethylene, as the two valencies cannot remain free.

ETHYLENE, C_2H_4 (Ethene), $H_2C = CH_2$. This is a gas, becoming liquid at $-103°$ and solid at $-169°$, or liquid at $0°$ under 44 atmos. pressure. It is very slightly soluble in water or alcohol. It has a somewhat sweet smell and burns with a luminous flame ; indeed, illuminating gas, which contains 2 to 3 per cent. of ethylene, owes part of its luminosity to this gas. When mixed with 2 vols. of chlorine it burns with a dark-red flame, carbon being deposited and HCl formed. At a red heat it yields C, CH_4, C_2H_6, C_2H_2, &c. ; with hydrogen in presence of spongy platinum or, better, powdered nickel at 300°, it is converted into ethane.

It is prepared in the laboratory by heating alcohol with excess of sulphuric acid ; as an intermediate product, ethyl-sulphuric acid is formed, this giving ethylene when heated : $C_2H_5{\cdot}OH + H_2SO_4 = H_2O + C_2H_5HSO_4$; $C_2H_5HSO_4 = H_2SO_4 + C_2H_4$. Pure ethylene is obtained (1) by passing a mixture of carbon monoxide and hydrogen over finely divided nickel or platinum at 100° : $2CO + 2H_2 = C_2H_4 + 2H_2O$; (2) by dropping alcohol on to phosphoric acid at 200–220° ; or (3) from ethylene bromide and a copper zinc couple.

PROPYLENE, C_3H_6 (Propene), $CH_2{=}CH{-}CH_3$. This can be prepared by heating glycerol with zinc dust or from isopropyl iodide and potassium hydroxide. It is a gas which liquefies at $-48°$ and is isomeric with trimethylene.

BUTYLENES, C_4H_8 (Butenes). Three isomerides, the α, β, and γ, are known, and are obtained by treating normal, secondary, and tertiary butylene iodides respectively with potassium hydroxide :

$CH_2{=}CH{-}CH_2{-}CH_3$	$CH_3{-}CH{=}CH{-}CH_3$	$\begin{matrix}CH_3\\CH_3\end{matrix}{>}C{=}CH_2$
Butene-1 (α-butylene)	Butene-2 (β-butylene)	Methylpropene (isobutylene)

Tetramethylene or cyclobutane is isomeric with the butylenes.

AMYLENES, C_5H_{10} (Pentenes). Of the various isomerides theoretically possible several have been prepared. By heating *fusel oil* (of distilleries) with zinc chloride, pentanes and various isomeric amylenes are formed which can be separated by means of the different velocities with which HI is added to them, or by the property possessed by some of them of dissolving in the cold in a mixture in equal parts of concentrated sulphuric acid and water, forming amylsulphuric acid, whilst the others either do not react or give condensation products (di- and triamylenes).

CEROTENE, $C_{27}H_{54}$, and MELENE, $C_{30}H_{60}$, are similar to paraffin, and are obtained by distilling Chinese wax or beeswax.

II. HYDROCARBONS OF THE SERIES, C_nH_{2n-2}

A. With Two Double Linkings (Diolefines or Allenes)

Of the few known terms of this series, the first and best investigated is ALLENE, $H_2C:C:CH_2$ (*propandiene*): this is a colourless gas which differs from its isomeride allylene in not forming metallic derivatives; it is obtained by eliminating one atom of bromine from tribromopropane by means of potassium hydroxide and the remaining two by zinc dust, its constitution being thus rendered evident:

$$CH_2Br\cdot CHBr\cdot CH_2Br \rightarrow CH_2:CBr\cdot CH_2Br \rightarrow CH_2:C:CH_2.$$

ERYTHRENE, C_4H_6 (Pyrrolilene or Butane-1:3-diene), $CH_2:CH\cdot CH:CH_2$, is a gas found in illuminating gas, and when heated with formic acid gives *erythritol.*

ISOPRENE, C_5H_8, boils at 37° and is obtained by distilling rubber. On the other hand, with concentrated HCl, it condenses, regenerating *rubber* or forming *terpenes*, $C_{10}H_{16}$, $C_{15}H_{24}$, &c. Since *dimethylallene*, $\frac{CH_3}{CH_3}{>}C:C:CH_2$, gives, with 2HBr, a dibromide, $\frac{CH_3}{CH_3}{>}CBr\cdot CH_2\cdot CH_2\cdot Br$, which is identical with that obtained from isoprene + 2HBr, the constitution of isoprene must be: $\frac{CH_2}{CH_3}{>}C\cdot CH:CH_2.$

The normal isomeride PIPERYLENE, $CH_2:CH\cdot CH_2\cdot CH:CH_2$ (Pentane-1:4-diene) boils at 42° and is obtained from *piperidine.*

DIALLYL, C_6H_{10} (Hexine), is prepared by the general reaction—the action of sodium on allyl iodide—which indicates its constitution:

$$2CH_2:CH\cdot CH_2I + 2Na = CH_2:CH\cdot CH_2\cdot CH_2\cdot CH:CH_2 + 2NaI.$$

CONYLENE, C_8H_{14} (1:4-octadiene), $CH_2:CH\cdot CH_2\cdot CH:CH_2\cdot CH_2\cdot CH_3$, boils at 126° and is obtained from *coniine.*

B. Hydrocarbons with Triple Linkings (Acetylene Series)

The most important members of this series are:

Acetylene, C_2H_2 (ethine), $HC\equiv CH$, gas.

Allylene, C_3H_4 (propine), $CH_3\cdot C\equiv CH$, gas.

Crotonylene, C_4H_6 (2-butine or dimethylacetylene), $CH_3\cdot C\vdots C\cdot CH_3$, boils at 27°.

Ethylacetylene, C_4H_6 (3-butine), $CH_3\cdot CH_2\cdot C\vdots CH$, boils at 18°.

Methylethylacetylene, C_5H_8 (3-pentine), $CH_3\cdot CH_2\cdot C\vdots C\cdot CH_3$, boils at 55°.

n-Propylacetylene, C_5H_8 (4-pentine), $CH_3\cdot CH_2\cdot CH_2\cdot C\vdots CH$, boils at 48°.

Isopropylacetylene, C_5H_8 (3-methyl-1-butine), $\frac{CH_3}{CH_3}{>}CH\cdot C\vdots CH$, boils at 28°

Several of these compounds (the first three) are formed during the dry distillation of coal and other complex substances, and are hence found in lighting gas.

In the laboratory they are obtained by the following methods:

(*a*) By electrolysing acids of the fumaric acid series (*see later*):

$$COOH\cdot CH\vdots CH\cdot COOH = H_2 + 2CO_2 + HC\vdots CH.$$

(*b*) By heating with alcoholic potash the halogenated compounds (best the bromo-derivatives) $C_nH_{2n}X_2$ and $C_nH_{2n-2}X_2$, gradual elimination of halogen hydracid (of HBr or, in presence of KOH, of KBr and H_2O) occurs:

$$C_2H_4Br_2 = HBr + C_2H_3Br \longrightarrow HBr + C_2H_2.$$

In general, starting from the saturated hydrocarbons, C_nH_{2n+2}, *the action of halogen and elimination of halogen hydracid gives an unsaturated hydrocarbon,* C_nH_{2n}; *addition of halogen to this and subsequent removal of halogen hydracid gives a still less saturated hydrocarbon,* C_nH_{2n-2}, *and so on.*

Elimination of 2HCl from the compounds $C_nH_{2n}Cl_2$, obtained from aldehydes or from certain ketones (methylketones, $C_nH_{2n+1}\cdot CO\cdot CH_3$) by the action of PCl_5, yields always a trebly linked compound, in which, however, one of the carbon atoms is always united to a single, characteristic hydrogen atom: $—C\equiv CH$; for example, acetaldehyde gives ethylidene chloride, $CH_3\cdot CHCl_2$, which then yields $2HCl + CH \vdots CH$; while acetone, $CH_3\cdot CO\cdot CH_3$, gives chloroacetone $CH_3\cdot CCl_2\cdot CH_3$, and this $2HCl + CH_3\cdot C\equiv CH$, the elimination of halogen hydracid never occurring in such a way as to give compounds with two double linkings, such as $CH_2 : C : CH_2$.

Acetylene derivatives are also obtained by heating the acids of the propiolic series (*see later*).

Compounds with this characteristic hydrogen atom $—C\equiv CH$ have a feebly acid character and form solid metallic derivatives (*acetylides*) when treated with an ammoniacal solution of copper chloride or silver nitrate: *copper acetylide*, $Cu\cdot C \vdots C\cdot Cu, H_2O$, having a reddish brown colour and apparently the constitution, $Cu_2CH\cdot CHO$, since with hydrogen peroxide it gives *acetaldehyde*, $CH_3\cdot CHO$ (Makowka, 1908); and *silver acetylide*, $AgC \vdots CAg$, which is white and insoluble in water or ammonia and, in the dry state, is extremely explosive, simple rubbing being sufficient to explode it. With hydrochloric acid it regenerates acetylene in a pure state.

The proof that it is the characteristic hydrogen atom which is replaced by metals lies in the fact that acetylene derivatives from other ketones (not from methylketones) do not give metallic acetylides:

$$CH_3\cdot CH_2\cdot CO\cdot CH_2\cdot CH_3 \longrightarrow CH_3\cdot CH_2\cdot CCl_2\cdot CH_2\cdot CH_3 \longrightarrow$$
$$2HCl + CH_3\cdot C \vdots C\cdot CH_2\cdot CH_3.$$

Four atoms of a halogen or of hydrogen can be added to the hydrocarbons of the acetylene series, saturated compounds being formed; but as a rule only two atoms are readily added, although under the action of light four halogen atoms can be added almost always.

The compounds of the olefine series can, however, be distinguished from those of the acetylene series by means of the *ozone reaction*, since compounds with a triple linking do not fix ozone at all (Molinari).

The hydrocarbons of the acetylene series take up a molecule of water in presence of mercury salts, giving rise to complex mercuric compounds, which, with HCl, give as final product an aldehyde or ketone of the saturated series—$CH_3\cdot C \vdots CH$ (allylene) $+ H_2O = CH_3\cdot CO\cdot CH_3$ (acetone) or $CH \vdots CH + H_2O = CH_3\cdot CHO$ (acetaldehyde). This last reaction serves to illustrate the transformation of inorganic into organic substances (*see later*, p. 108).

In the acetylene series, also, condensation or polymerisation is possible, three molecules of acetylene, on heating, yielding benzene C_6H_6; three mols. of dimethylacetylene, C_4H_6, giving, with concentrated sulphuric acid, *hexamethylbenzene*, $C_6(CH_3)_6$, and allylene C_3H_4 similarly yielding *trimethylbenzene* (*mesitylene*) $C_6H_3(CH_3)_3$.

In the higher compounds, the position of the triple bond is deduced from the oxidation products, since, as with substances with a double linking, the breaking of the chain occurs at the multiple linking.

When certain acetylene derivatives, *e.g.* $XC \equiv C \cdot CH_3$, are heated with sodium, the triple bond changes its position, the products being sodium derivatives of isomeric hydrocarbons, $X \cdot CH_2 \cdot C : CH$ (these give metallic acetylides, but the original compounds do not); when these are heated with alcoholic potash, the reverse change occurs.

ACETYLENE, C_2H_2 (Ethine), $HC : CH$. Without having isolated or characterised this compound, Davy obtained it in 1839 in a very impure condition, by treating with water the product obtained by heating together potassium carbonate and carbon, which should yield potassium. Berthelot first obtained it pure (and named it) in 1859, by passing ethylene or alcohol or ether vapour through a red-hot tube; he prepared it also by means of a voltaic arc passing between two carbons in an atmosphere of hydrogen. In 1862, Wöhler prepared it by treating calcium carbide (obtained by heating carbon with an alloy of zinc and calcium) with water.

It is formed in the incomplete combustion of various hydrocarbons and of illuminating gas (*e.g.* in the flame of a bunsen burner alight at the bottom).

But the industrial preparation of acetylene has assumed great and unforeseen practical importance since 1870, when it became possible to prepare *calcium carbide* on an enormous industrial scale by means of the electric furnace (*see* Calcium Carbide Industry, vol. i, p. 504):

$$\left.\begin{matrix} C \\ \| \! | \\ C \end{matrix}\right> Ca + 2H_2O = Ca(OH)_2 + HC : CH.$$

Acetylene is a colourless gas, sp. gr. 0·92 (1 litre weighs 1·165 grm.) with a pleasant odour when pure and a disagreeable one when impure (as usually obtained). At $+ 1^\circ$ under a pressure of 48 atmos. it forms a highly refractive, mobile, colourless liquid, sp. gr. 0·451, and, on evaporating rapidly, partially solidifies in the form of snow, m.pt. -81°.

One volume of acetylene gas dissolves in 1·1 vol. of water, or in $\frac{1}{6}$ vol. of alcohol or in 20 vols. of saturated salt solution; 1 litre of acetone dissolves 24 litres of acetylene, or 300 litres at 12 atmos., or about 2000 litres at -80°, its volume being then increased fourfold. Permanganate oxidises it giving oxalic acid, and chromic acid acetic acid.

It is an endothermic compound, requiring for its formation from its elements, 61,000 cals.; it is hence very unstable and is readily decomposed by the detonation of a mercury fulminate cap or by an electric discharge, developing as much heat as an equal volume of hydrogen on conversion into water. The explosion takes place much more readily and is much more dangerous with the compressed gas and still more so with the liquid.

Acetylene decomposes at 780° and, when mixed with air, ignites at 480°. One cubic metre (1·165 kilo) of acetylene, in burning, develops 14,350 Cals. (12,300 Cals. per kilo), whilst ordinary coal-gas gives about 5000 Cals.

When mixed with air or, better, with oxygen it forms a *detonating mixture* which explodes with great energy in contact with an ignited body. The explosion is violent even with 1 vol. of acetylene and 40 vols. of air; it reaches its maximum violence with 1 vol. of the gas and 12 vols. of air (2·5 vols. of oxygen), whilst scarcely any explosion but mere burning takes place with 1 vol. of acetylene and 1·3 vol. of air (as has been already stated on p. 33, ordinary illuminating gas only explodes when at least 1 vol. is present to about 20 vols. of air).

Explosive mixtures of acetylene are more dangerous than those of coal-gas

owing to the greater speed of propagation of the explosion (*e.g.* with 1 vol. of acetylene and 40 of air), the explosive force being thus increased (*see* section on Explosives); further, acetylene contains less hydrogen and hence forms less water, the condensation of the gases resulting from the explosion being consequently smaller. The wide limits of the explosive mixtures (from 2·4 to 130 vols. of acetylene per 100 vols. of air) are explained by the fact that this gas, being an endothermic compound, reacts or decomposes with great facility.

In contact with copper, bronze, silver, &c., acetylene readily forms explosive acetylides (*see* p. 91).[1]

It was at first thought that acetylene, like carbon monoxide, was poisonous, but experiments made during the last few years have shown that animals do not die in an atmosphere containing 9 per cent. or, in some cases, even 20 per cent. of the gas. When, however, the acetylene is highly contaminated with sulphides and phosphides, it may be poisonous.

With an ordinary gas-jet, acetylene burns with a reddish, smoky flame; but by passing the gas at a pressure of 60 mm. through two jets nearly meeting at an angle, a white, highly luminous, fan-shaped flame is obtained without the dark middle portion of the ordinary bat's-wing coal-gas flame.

One kilo of chemically pure calcium carbide should yield theoretically 349 litres of acetylene, and good commercial carbide yields practically 300 litres. The luminosity of acetylene in comparison with that of other substances has already been referred to on p. 57. A proportion of 2 vols. of air to 3 of acetylene gives the maximum luminosity, and at the present time special incandescent mantles are made for use with acetylene.

The impurities present in ordinary acetylene (98–99 per cent. purity) are: N, NH_3, CO, H_2S and PH_3, the last three of which are poisonous. The gas is purified by passing it through an *acid* solution of a metallic salt.

Lunge and Cederkreutz recommend chloride of lime (hypochlorite) for purifying acetylene, care being taken that the mass does not heat, as this would be dangerous. Latterly it has been suggested to fix the PH_3 by passing the gas through concentrated sulphuric acid (64° Bé.) saturated with As_2O_3. A good purifying material is made by preparing a paste of calcium hypochlorite, quicklime, sodium silicate and powdered calcium carbide, this remaining porous when allowed to dry in the air.

The use of liquid acetylene would be very convenient, but is highly dangerous, since a sharp blow or other accident might easily produce a terrible explosion.

It is still too expensive to employ in place of benzene for carburetting coal-gas. Dissolved in acetone, which dissolves a large quantity of it (*vide supra*), it is used to great advantage for the *oxy-acetylene blowpipe* in place of oxy-hydrogen. With the latter, for every cubic metre of oxygen 4 cu. metres of hydrogen are used practically (theoretically 2 cu. metres), whilst the same amount of oxygen burns with 600 litres of acetylene (theoretically 400 litres), which costs much less than 4 cu. metres of hydrogen. The oxy-acetylene flame exhibits at the centre a shining point, which has a temperature of 2800–3000°, and to fuse iron sheets 1 mm. thick requires 50–75 litres of acetylene, while in an hour sheets 5 mm. in thickness can be melted.

With a slight excess of oxygen large tubes are easily cut and steel blocks perforated.

Acetylene dissolved in acetone, especially if the solution is absorbed by porous material, is not at all dangerous and can be transported in iron cylinders.

The hope of manufacturing synthetic alcohol economically from acetylene has died out. Even for motors it is still too dear to use. Acetylene can, however, be used conveniently with a rational plant and relatively small gasometers connected with iron tubes which carry the gas direct to the burners (when prepared from pure carbide); but it is necessary to avoid the use of copper or bronze in any part of the gasometers, pipes

[1] The ready formation of metallic acetylides, especially that of copper, led Erdmann (1907) to devise a rapid and exact analytical method for the direct quantitative precipitation of copper from any solution and in presence of any metals (except Ag, Hg, Au, Pd, and Os, which must be previously eliminated); the feebly alkaline solution of the copper salt is reduced until decolorised with hydroxylamine hydrochloride, C_2H_2 being then passed through and the precipitated copper acetylide collected on a filter, washed with water and pumped off; together with the filter-paper it is introduced into a porcelain crucible, treated with 10 to 15 c.c. of dilute nitric acid (sp. gr. 1·15) and eight to ten drops of concentrated nitric acid (sp. gr. 1·52), dried on a water-bath, heated rapidly to redness and weighed as CuO. The acetylene used for this precipitation should be washed with lead acetate solution.

and taps, in order to avoid explosions, which are almost always due to the formation of copper acetylide.[1]

In testing the purity of acetylene the only quantitative determination usually made is that of the hydrogen phosphide, which should not occur in greater proportion than 1 grm. per cubic metre, since, besides being poisonous and having an unpleasant smell, it facilitates the formation of explosive metallic acetylides. (The estimation of the impurities in carbide is described in vol. i, p. 505.)

III. HYDROCARBONS OF THE SERIES C_nH_{2n-4} and C_nH_{2n-6}

DIACETYLENE, C_4H_2 (Butandiine), CH ⋮ C C ⋮ CH, is a gas and forms the usual metallic acetylides.

DIPROPARGYL, C_6H_6 (Hexan-1 : 5-diine), CH ⋮ C·CH_2·CH_2·C ⋮ CH, is isomeric with benzene, boils at 85°, and can take up 8 atoms of bromine. It is obtained from diallyl and readily forms metallic acetylides.

HEXAN-3 : 4-DIINE, CH_3·C . C·C ⋮ C CH_3, is also isomeric with benzene.

BB. HALOGEN DERIVATIVES OF THE HYDROCARBONS

The Table on page 95 summarises the physical properties of the more important halogen derivatives of the hydrocarbons, the first column giving the hydrocarbon *residue* (*alkyl*) united with the halogen.

I. HALOGEN DERIVATIVES OF SATURATED HYDROCARBONS

PROPERTIES. Very few are gases, several are liquids and, those which contain many atoms in the molecule are solids. The iodo-compounds boil at higher temperatures than the corresponding bromo- and chloro-compounds. They are very slightly, if at all, soluble in water, but are readily soluble in alcohol, ether, and glacial acetic acid.

Most of them burn easily, and ethyl and methyl chlorides colour the edges of the flame green. Some of them, containing few carbon atoms, produce *anæsthesia*, *e.g.* $CHCl_3$, CH_2Cl_2, $C_2H_3Cl_3$, C_2H_5Br, C_2H_5Cl.

Generally they do not react with silver nitrate, since these compounds, in solution, are not dissociated and do not give free halogen ions (*see* vol. i, p. 91 *et seq.*). In alcoholic solution, ethyl iodide gives a little precipitate in the cold, and ethyl bromide in the hot, whilst the chloride gives no precipitate at all, with silver nitrate.

The bromo- and iodo-compounds exhibit great reactivity and effect the most varied and interesting reactions and syntheses ; methyl iodide reacts the most readily of all, since the reactivity diminishes with increase of molecular weight.

The halogens of these compounds can easily be replaced by H (by sodium-amalgam, or zinc dust and hydrochloric or acetic acid).

These derivatives can, to some extent, be transformed one into the other, *e.g.* the chlorides into iodides by treatment with KI or CaI_2, and the iodides into the fluorides (more volatile than the chlorides) by means of silver fluoride.

[1] The numerous types of apparatus for generating acetylene may be divided into three groups :

(1) Those where the carbide and water are in separate vessels communicating by a tube furnished with a tap which automatically opens more or less and so diminishes or increases the supply of the gas. To prevent the carbide, or rather the lime formed, from holding water and generating gas even after the tap is closed, the carbide is impregnated with an indifferent substance, *e.g.* paraffin, stearin, oil, sugar (to dissolve the lime as calcium saccharate), &c. One inconvenience of this procedure is that at some places the carbide, in presence of little water, becomes excessively heated and may produce an explosion, which is dangerous if the gas is under pressure.

(2) Those where the carbide is suspended at a certain part of the vessel containing the water ; acetylene is then generated when the level of the water rises to the carbide and ceases automatically when it falls.

(3) Those where the carbide and water are separated, a small quantity of carbide being dropped into excess of water. This would be the most rational method, but is perhaps not the most convenient owing to the difficulty of powdering the carbide (often very hard) without allowing it to absorb moisture.

Alkyl	Names of the Alkyls and Isomerides	Chlorides		Bromides		Iodides	
		B.-pt	Sp. gr.	B -pt.	Sp. gr.	B.-pt.	Sp. gr.
	(*a*) SATURATED DERIVATIVES						
	(1) *Monosubstituted*						
CH_3	Methyl	− 23 7°	0·952 (0°)	+ 4·5°	1·732 (0°)	+ 45°	2·293 (18°)
C_2H_5	Ethyl	+ 12 2°	0 918 (0°)	38·4°	1·468 (13°)	+ 72·3°	1·944 (14°)
C_3H_7	n-Propyl	+ 46 5°	0 912 (0°)	71°	1 383 (0°)	102 5°	1·786 (0°)
	Isopropyl	36 5°	0 882 (0°)	60°	1·340° (0°)	89°	1·744 (0°)
C_1H_9	n-Butyl (primary)	78°	0 907 (0°)	101°	1 305 (0°)	130°	1·643 (0°)
	Isobutyl	68·5°	0 895 (0°)	92°	1·204 (16°)	119°	1·640 (0°)
	sec.-Butyl	—	—	—	—	119–120°	1·626 (0°)
	tert.-Butyl	55°	0·866 (0°)	72°	1 215 (20°)	100°	1 571 (0°)
C_5H_{11}	n-Amyl (primary)	107°	0 901 (0°)	129°	1·246 (0°)	156°	1 543 (0°)
	Isoamyl, $(CH_3)_2$ CH· CH_2 CH_2·X	101°	0 893 (0°)	121°	1 236 (0°)	148°	1·468 (0°)
	tertiary-Butylmethyl $(CH_3)_3C$ CH_2·X	—	0 879 (0°)	—	1·225 (0°)	—	1·050? (0°)
	active-Amyl $(CH_3)(C_2H_5)CH\cdot CH_2\cdot X$	97 99°	0·886 (15°)	118–120°	1·221 (20°)	148°	1·524 (20°)
C_6H_{13}	n-Hexyl (primary)	134°	0 892 (16°)	156°	1·193 (0°)	182°	1 461 (0°)
	n-Hexyl (secondary)	—	—	144°	—	168°	1·453 (0°)
C_7H_{15}	n-Heptyl (primary)	159°	0 881 (16°)	179°	1·113 (16°)	201°	1·386 (16°)
C_8H_{17}	n-Octyl (primary)	180°	0 880 (16°)	199°	1·116 (16°)	221°	1·345 (16°)
	(2) *Disubstituted*						
$>CH_2$	Methylene, CH_2X_2	42°	—	97°	—	180°	—
$-CH_2\cdot CH_2-$	Ethylene	84°	—	131°	—	—	—
CH_3 $CH_2<$	Ethylidene (or ethydene)	57°	—	108°	—	—	—
	(3) *Trisubstituted*						
	CHX_3 (chloroform, bromoform, iodoform)	61°	—	151°	—	solid m pt.119°	—
	CH_3 CCl_3 methyl chloroform (α-trichloroethane)	74°	—	188°	—	—	—
	$CH_2Cl\cdot CHCl_2$ (β-trichloroethane)	114°	—	220°	—	—	—
	CH_2X $CHX\cdot CH_2X$ (trichlorohydrin, tribromohydrin)	158°	—	—	—	—	—
	(4) *Polysubstituted*						
	CX_4 (carbon tetrachloride, iodide)	77°	—	—	—	solid	—
	C_2Cl_6 perchloroethane	solid m.pt. 187°	—	—	—	—	—
	(*b*) UNSATURATED DERIVATIVES						
	(1) *Ethylenic series*						
$CH_2:CH\cdot X$	Vinyl chloride, &c.	− 18°	—	23°	—	56°	—
$C_3H_5\cdot X$	Allyl	46°	—	70°	—	101°	—
$C_2H_2:X_2$	Dichloroethylene	55°	—	—	—	—	—
$C_2H\cdot X_3$	Trichloroethylene	88°	—	—	—	—	—
$C_2 . X_4$	Tetrachloroethylene	121°	—	—	—	—	—
	(2) *Acetylene series*						
HC . CX	Monochloro- and monobromo-acetylene	gas	—	gas	—	—	—

METHODS OF PREPARATION. (*a*) By the action of halogens on saturated hydrocarbons : chlorine and bromine react directly at the ordinary temperature on the gaseous hydrocarbons, and on heating with the liquid ones.

The first halogen atom is fixed more readily than the succeeding ones, and the addition of iodine facilitates the reaction with bromine and chlorine, since the iodine forms, for example, ICl_3, which readily gives nascent chlorine, $ICl_3 = ICl + Cl_2$ (*i.e.* it acts like $SbCl_5$, which yields $SbCl_3 + Cl_2$). By saturating with chlorine and heating under pressure energetic chlorinations may be effected.

Methane, ethane, propane, &c., exchange their hydrogen atoms one by

one for chlorine atoms, the completely substituted compounds (C_2Cl_6, C_3Cl_8, &c., and especially the higher ones), on further energetic chlorination, being resolved into other completely chlorinated compounds containing less numbers of carbon atoms: $C_2Cl_6 + Cl_2 = 2CCl_4$; $C_3Cl_8 + Cl_2 = C_2Cl_6 + CCl_4$, a little hexachlorobenzene, &c., being always formed as well.

Iodine scarcely ever acts directly on the hydrocarbons, since the HI formed acts in the opposite sense on the iodo-products. The reaction proceeds only in presence of iodic acid or mercuric oxide, which fixes the hydriodic acid as it is formed.

The iodo-compounds are easily obtained from zinc-alkyls and iodine.

When the halogens act directly, the more energetic (F or Cl) replaces the weaker (Br or I). The iodo-compounds may, however, be easily obtained by preparing first the magnesium compounds of the alkyl chlorides or bromides and treating these with iodine:

$$\text{Alkyl–Mg–Cl} + I_2 = \text{Alkyl–I} + MgICl.$$

(*b*) *Unsaturated hydrocarbons*, with the halogen hydracids, give saturated monosubstituted derivatives: $C_2H_4 + HBr = C_2H_5Br$, ethyl bromide, &c.; if the halogens act directly, disubstituted saturated products are obtained: $C_2H_4 + Cl_2 = C_2H_4Cl_2$, ethylene dichloride.

Propylene, $CH\cdot{}_3CH:CH_2$, reacts with HI giving *isopropyl iodide*, $CH_3\cdot CHI\cdot CH_3$, which is decomposed by alcoholic potash, yielding propylene; but *normal propyl iodide*, $CH_3\cdot CH_2\cdot CH_2I$, which also yields propylene when HI is removed from it, can thus be converted into isopropyl iodide.

Similar behaviour is exhibited by the butyl iodides.

The halogen always goes to the carbon atom united with the lesser number of hydrogen atoms: $CH_3\cdot CH:CH_2 + HI = CH_3\cdot CHI\cdot CH_3$.

(*c*) The *alcohols* $C_nH_{2n+1}OH$ with the halogen hydracids give: $C_nH_{2n+1}OH + HBr = H_2O + C_nH_{2n+1}Br$, but the reverse action also proceeds and to limit this, excess of the halogen hydracid is used and the water formed is fixed, *e.g.* by addition of zinc chloride.

Further, the chlorine of the phosphorus chlorides also replaces hydroxyl: $PCl_3 + 3C_2H_5OH = P(OH)_3 + 3C_2H_5Cl$, or, better, $PCl_5 + C_2H_5OH = POCl_3 + HCl + C_2H_5Cl$. This reaction is of importance for the preparation of the bromo- and iodo-compounds: $3CH_3\cdot OH + P + 3I = 3CH_3I + H_3PO_3$; the bromine or iodine first acts on the phosphorus to form PBr_3 or PI_3, this then reacting with the alcohol.

The polyhydric alcohols act in the same way; for example, glycerol, $C_3H_5(OH)_3$ reacts with PCl_5 giving trichlorohydrin, $CH_2Cl\cdot CHCl\cdot CH_2Cl$.

The resulting halogenated products are easily separated by distillation, as the phosphoric acid does not distil. In these, as in most other chemical reactions, secondary products are always formed; these are often very complex and form viscous resins of unknown composition.

(*d*) The *aldehydes* and *ketones* yield disubstituted products: for example, ethylidene chloride, $CH_3\cdot CHCl_2$, is obtained from acetaldehyde, $CH_3\cdot CHO$, and dichloropropane, $CH_3\cdot CCl_2\cdot CH_3$, from acetone, $CH_3\cdot CO\cdot CH_3$, by the action of PCl_5.

METHYL CHLORIDE (Chloromethane), CH_3Cl. This is prepared by passing hydrogen chloride into boiling methyl alcohol containing half its weight of zinc chloride in solution, or by heating 1 part of methyl alcohol with 3 parts of concentrated sulphuric acid and 2 parts of concentrated hydrochloric acid. Industrially it can be obtained by heating methyl alcohol and crude, concentrated hydrochloric acid together in an autoclave.

It is also obtained to-day in appreciable quantity, by the old Vincent process, from the final residues of the beet-sugar industry, which are evaporated

and then dry-distilled. In this way an abundant quantity of trimethylamine is formed; this is neutralised with HCl, and the hydrochloride distilled at 300°. A regular evolution of methyl chloride and trimethylamine is thus obtained: $\underset{\text{Trimethylamine hydrochloride}}{3N(CH_3)_3HCl} = 2CH_3Cl + \underset{\text{Trimethylamine}}{2N(CH_3)_3} + \underset{\text{Methylamine hydrochloride (residue)}}{CH_3 \cdot NH_2 \cdot HCl}$.

The chloromethane, distilled as a gas, is purified with HCl, dried with $CaCl_2$, and liquefied in steel cylinders under pressure, just as is done with carbon dioxide (vol. i, p. 382).

It is a colourless gas of ethereal odour, and at $-23 \cdot 7°$ becomes liquid, then having a sp. gr. 0·952 (at 0°). Water dissolves one-fourth of its volume, and alcohol rather more. It burns with a green-edged flame.

In the liquefied condition it is used as a local anæsthetic; it is used also to extract perfumes from flowers, and in considerable quantities for the manufacture of dyestuffs (methyl green), especially for methylation; but the greatest amount is employed in cooling machines. In France there are about 100 ice-machines which use methyl chloride instead of liquefied NH_3, CO_2, or SO_2. In brass cylinders containing from 1 to 30 kilos it is sold at 11*s*. to 14*s*. 6*d*. per kilo, in addition to the cost of the cylinder, which is 20*s*. for the 1-kilo, 25*s*. 6*d*. for the 3-kilo, and £3 16*s*. for the 30-kilo size.

METHYL IODIDE, CH_3I, is prepared from methyl alcohol, phosphorus, and iodine as described later for ethyl iodide. It is a liquid of sp. gr. 2·293, boiling at 45°; with excess of water at 100° it is decomposed into hydrogen iodide and methyl alcohol.

ETHYL CHLORIDE (Chloroethane), C_2H_5Cl, was termed by Basil Valentine "Spiritus salis et vini," or *spirit of sweet wine*. It is obtained from ethane and chlorine, or by passing hydrogen chloride into a solution of zinc chloride and ethyl alcohol. It is also formed as a secondary product in the manufacture of chloral. It boils at $+12 \cdot 2°$ and burns with a flame having green edges. It is a local anæsthetic and is soluble in alcohol, but only slightly so in water. It costs from 1*s*. 7*d*. to 4*s*. per kilo in metal cylinders containing 1 to 30 kilos.

ETHYL IODIDE, C_2H_5I, is prepared by digesting 10 grms. of red phosphorus with 80 grms. of absolute alcohol for 12 hours and gradually adding 100 grms. of iodine; the mixture is then heated for 2 hours under a reflux condenser and the ethyl iodide distilled on the water-bath, washed with dilute alkali and with water, and dried by means of calcium chloride. According to Ger. Pat. 175,209, ethyl iodide is obtained quantitatively if diethyl sulphate is slowly added to the calculated amount of hot potassium iodide solution. It boils at 72·3° and has the sp. gr. 1·944 (at 14°); it is highly refractive and dissolves in alcohol or ether. It decomposes when heated with water at 100°. Chlorine converts it into ethyl chloride and bromine into ethyl bromide. In the light it slowly decomposes with separation of iodine, which colours the liquid brown, but it remains colourless in presence of a drop of mercury. It is used as an inhalation for the treatment of asthma. It costs about 28*s*. to 32*s*. per kilo.

ETHYL FLUORIDE, C_2H_5F, is liquid at $-48°$, burns with a blue flame, and does not attack glass.

From **PROPANE** two series of isomeric compounds are derived: $CH_3 \cdot CH_2 \cdot CH_2X$, prepared from normal propyl alcohol, and $CH_2 \cdot CHX \cdot CH_3$, derived from isopropyl alcohol, and hence from acetone.

ISOPROPYL IODIDE (Iodo-2-propane), $CH_3 \cdot CHI \cdot CH_3$, is obtained from glycerol, phosphorus and iodine, small amounts of allyl iodide and propylene being also formed.

The butyl compounds occur in four isomeric modifications:

NORMAL BUTYL IODIDE (Iodo-1-butane), $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2I$.

SECONDARY BUTYL IODIDE (Iodo-2-butane), $CH_3 \cdot CH_2 \cdot CHI \cdot CH_3$.

ISOBUTYL IODIDE (Methyl-2-iodo-3-propane), $\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}CH \cdot CHI$.

TERTIARY BUTYL IODIDE (Methyl-2-iodo-2-propane), $\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}CI \cdot CH_3$.

The constitutions of the four isomerides are deduced from those of the corresponding butyl alcohols from which they are obtained by the action of hydriodic acid.

Of the **AMYL** derivatives eight isomerides are known.

METHYLENE CHLORIDE (Dichloromethane), CH_2Cl_2, *bromide* and *iodide* (see Table, p. 95).

ETHYLENE COMPOUNDS, $CH_2X \cdot CH_2X$, are formed from ethylene by the addition of halogens or from glycol, $C_2H_4(OH)_2$ and halogen hydracids.

ETHYLIDENE (or Ethydene) **COMPOUNDS**, $CH_3 \cdot CHX_2$, are obtained by substituting the oxygen of the aldehydes by halogens.

ETHYLENE CHLORIDE (Dichloro-1 : 2-ethane), $CH_2Cl \cdot CH_2Cl$ (*Dutch liquid*), boils at 84°. The **IODIDE, BROMIDE,** and **CHLORIDE** with alcoholic potash give acetylene and glycol.

ETHYLIDENE CHLORIDE (Ethydene chloride or Dichloro-1 : 1-ethane), $CH_3 \cdot CHCl_2$, is obtained from aldehyde and phosgene: $CH_3 \cdot CHO + COCl_2 = CO_2 + CH_3 \cdot CHCl_2$, chloral (*which see*) being also formed ; it boils at 57°.

CHLOROFORM (Trichloromethane), $CHCl_3$. Chloroform was discovered by Liebig and Souberain and its constitution shown by Liebig in 1835.

It is prepared from (1) ethyl alcohol or (2) acetone, by heating with chloride of lime and water: (1) $4C_2H_5OH + 16CaOCl_2 = 3H_2C_2O_4Ca$ (*calcium formate*) $+ 13CaCl_2 + 8H_2O + 2CHCl_3$; in this reaction there is always an appreciable evolution of CO_2, which appears to originate in the oxidation of the alcohol, and liberates HClO and so forms aldehyde and hence chloral, this, in presence of lime, yielding chloroform: $3C_2H_5OH + 8Ca(OCl)_2 = 2CHCl_3 + 3CaCO_3 + CO_2 + 8H_2O + 5CaCl_2$.

(2) $2CH_3 \cdot CO \cdot CH_3 + 3Ca(OCl)_2 = 2CH_3 \cdot CO \cdot CCl_3$ (*trichloro-acetone*) $+ 3Ca(OH)_3$; $2CH_3 \cdot CO \cdot CCl_3 + Ca(OH)_2 = Ca(C_2H_3O_2)_2$ (*calcium acetate*) $+ 2CHCl_3$.

In a very pure form for pharmaceutical use it is obtained by treating chloral with aqueous caustic soda solution, sodium formate being also formed :

$$CCl_3 \cdot C\begin{matrix} \diagup H \\ \diagdown O \end{matrix} + NaOH = CHCl_3 + H \cdot CO_2Na.$$

Chloroform can also be obtained industrially by reducing carbon tetrachloride with hydrogen in the hot : $CCl_4 + H_2 = HCl + CHCl_3$; the hydrogen necessary to treat 75 kilos of CCl_4 is given by 60 kilos of HCl at 22° Baumé and 50 kilos of zinc.

To obtain very pure chloroform from the impure product, Anschütz treats the latter with salicylic anhydride, $C_6H_4CO_2$, which forms a crystalline mass only with chloroform, $(C_6H_4CO_2)_4, 2CHCl_3$; this, after separation from the mother-liquor, is heated on the water-bath, when pure chloroform distils off.

It is a colourless liquid with a sweet ethereal smell and taste ; it dissolves only to a slight extent in water (0·7 per cent.), but is soluble in alcohol or ether. It boils at 61·2°, and its vapour pressure at 20° is 160 mm. of mercury ; its specific gravity is 1·5263 at 0° and 1·500 at 15°, referred to water at 4°.

It is non-inflammable, and it dissolves resins, rubber, fats, and iodine, with the last of which it gives violet solutions.

Exposed to light and air, it decomposes partially into Cl, HCl, and $COCl_2$, but it can be kept in yellow bottles, while that for pharmaceutical use keeps better if 1 per cent. of absolute alcohol is added.

It is the most efficacious *anæsthetic* (Simpson, 1848), but in some cases may cause death if not used with great care, since it acts on the heart ; to diminish this effect, it is mixed with atropine or morphine.[1]

[1] From coal-tar products various *anæsthetics* or *hypnotics* are produced synthetically, and these have been of great service to medicine, especially to surgery, rendering possible the execution of the most complicated operations without any pain to the patient. At first substances were used which produced *general anæsthesia* of the organism, but they were accompanied by many inconveniences, sometimes by fatal results.

Indeed, the anæsthetic is transported by the blood into contact with the higher nervous centres by which pain is felt, producing poisoning and paralysis of them often lasting for some time ; at the same time an influence is felt by the centres controlling the action of the heart and of respiration, this being the cause of the danger and disturbance produced by general anæsthesia. The nerve-currents start from the periphery, from the points where the surgical operation is to begin, and are transmitted to the brain, which transforms them into painful sensations,

In America, chloroform is used to render pigs insensible so as to kill them painlessly and to skin them more easily. Also, in fattening them, they are subjected to periodic inhalations of chloroform, which renders them more restful.

Chromic acid transforms chloroform into *phosgene* ($COCl_2$), whilst potassium amalgam gives acetylene. With potassium hydroxide, it gives potassium formate and chloride :

$$CHCl_3 + 4KOH = 3KCl + H \cdot CO_2K + 2H_2O.$$

With ammonia at a red heat, it gives hydrocyanic and hydrochloric acids :

$$CHCl_3 + NH_3 = HCN + 3HCl.$$

Pictet Chloroform is pure chloroform obtained from the commercial product by freezing it at −80° to −120° ; the impurities remain in the liquid, the crystals giving pure chloroform.

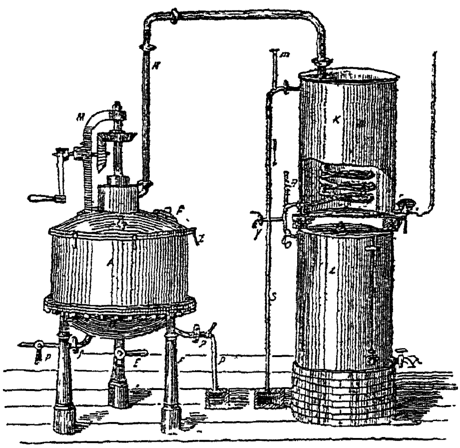


FIG. 102.

INDUSTRIAL PREPARATION. A considerable amount of chloroform is prepared even to-day from chloride of lime and alcohol, but the latter should not contain fusel oil. The reaction takes place in a double-bottomed iron boiler, *A* (Fig. 102), which contains a mechanical stirrer, *M*, and into which the chloride of lime, water, and alcohol are introduced through a large aperture, *F*, at the top. The heating is effected by a steam-coil, *Pp*, and cold water can be circulated through the jacketed bottom, when necessary, by means of another pipe not shown in the figure. To produce 100 kilos of chloroform 100 kilos of alcohol and 1300 kilos of chloride of lime (with 36 per cent. Cl) are actually used ; but in practice a large excess of alcohol—about ten times that really required by the reaction—is employed, but the excess is used up, since it is added all at once and the process then continued by gradually replacing the quantity that reacts.

An apparatus for producing 125 kilos of chloroform daily—with four charges of the apparatus in 24 hours—is charged first of all with 300 kilos of alcohol (96 per cent.) and 1300 litres of water, 400 kilos of chloride of lime being then added, in small quantities and with constant stirring ; the aperture *F* is then covered and the temperature raised to 40° by steam-heating. The steam is then shut off and the stirring continued until the temperature rises spontaneously to 60° (if this is exceeded, cold water is passed through the jacket). The mixing is then stopped and the chloroform, mixed with a little alcohol, begins to distil. The vapours are cooled and condensed in a coil, *Z*, placed in the tank, *K*, through which cold water circulates from *V* to *ms*. The mixed chloroform and alcohol is collected in a reservoir, *L*, with a graduated standpipe. When about 30 kilos of chloroform have distilled over, the stirrer is started again, and a little of the distillate

and it is by influencing the cerebral centres by anæsthetics that pain is avoided ; but anæsthesia ceases to be dangerous if the peripheral nervous centres at the beginning of the nerve-currents are paralysed without the latter reaching the brain. Thus *local anæsthesia* is much more rational and less dangerous, since the insensibility extends only to one organ or one region of the subject of the operation.

So that, to *chloroform, ether*, &c., was added, in 1885, *cocaine*, which paralyses only the sensitive peripheral nerves without influencing the motor nerves. By studying anæsthetic and hypnotic substances chemists were able to determine what specific atomic groups produced anæsthetic properties in a molecule. Thus, with many of these substances, it was found to be the hydroxyl group which induced sleep, especially when it is united to carbon joined at the same time to several alkyl groups ; replacement of the hydroxyl by other groups resulted in the disappearance of the anæsthetic properties. Also various amino-acid groups, under certain definite conditions, give rise to anæsthetics. To enumerate all the members of the vast group of anæsthetics which chemistry has placed at the disposal of surgery would be out of place here, but the following few examples may be mentioned : *α-eucaine, β-eucaine, orthoform, alipine, holocaine*, and, on the other hand, *sulphonal, trional, dormiol, hedonal, veronal*, &c. Other properties of anæsthetics are described in Part III, in the section on alkaloids.

collected from time to time from the tap, y, at the bottom of the condensing coil; when the addition of water to this no longer causes separation of chloroform at the bottom of the liquid, the remainder of the distillate obtained—finally the contents of the boiler are again heated with steam—is collected at y, communication with the reservoir, L, being shut off and the tap, O, closed. More or less dilute alcohol now distils over and the distillation is stopped when the distillate contains less than 2 to $2\frac{1}{2}$ per cent. of alcohol.

The total amount of alcohol (usually 260–265 kilos) in the alcoholic distillate (500–600 litres) is determined, and sufficient pure alcohol added to bring the total quantity up to 300 kilos; this dilute solution serves for the next operation, allowance being made for the water it contains. In this way the loss of alcohol is small.

The crude chloroform is washed and agitated with water (30 litres per 100 kilos) to remove the alcohol present, or, better, with lime-water or a weak soda solution, which removes also the small quantity of HCl that always forms. Finally, the liquid is agitated with concentrated sulphuric acid, thoroughly rewashed with water, dried over $CaCl_2$ and redistilled, the chloroform, passing over at 62–63°, being collected. Instead of alcohol, acetone is used by some manufacturers when it can be bought cheaply, and in that case 100 kilos of acetone yields up to 170 kilos of chloroform. According to Ger. Pat. 129,237, a good yield and continuous formation of chloroform are obtained by heating, in a vessel divided into a number of cells communicating at the bottom, alcohol (35° Bé) which has been previously chlorinated by means of chloride of lime and alkali in the hot.

During recent years the industrial preparation of chloroform has again been attempted by electrolysing an aqueous solution of KCl (20 per cent.) into which alcohol or acetone is slowly introduced. In this process 1 h p -hour is consumed to produce 40 grms. of chloroform.

Erlworthy and Lange (Fr. Pat. 354,291, 1905) propose to produce chloroform from methane and chlorine diluted with indifferent gases (N, CO_2) by subjecting the mixture to the action of light in suitable retorts: $CH_4 + 6Cl = 3HCl + CHCl_3$.

TESTS FOR CHLOROFORM. Minute quantities of chloroform can be detected by gently heating a little of the liquid with a few drops of aniline and of alcoholic potash solution, the characteristic repulsive odour of phenylcarbylamine (phenyl isocyanide) being formed. Pure chloroform for medicinal use should not be acid or give a precipitate with silver nitrate solution or redden potassium iodide solution; on evaporation it should not leave a residue of water or odorous substances, and it should not darken with concentrated sulphuric acid To test for the presence in it of carbon tetrachloride, 20 c.c. are treated with a solution of 3 drops of aniline in 5 c.c. of benzene; a turbidity or separation of crystals of phenylurea indicates with certainty the presence of the tetrachloride. To ascertain if it contains alcohol it is treated with a very dilute potassium permanganate solution, which is decolorised in presence of this impurity.

Its estimation is effected by treating a given weight with Fehling's solution (*see under* Sugar Analysis) and heating the mixture in a *closed* bottle on a water-bath for some hours (until the odour of chloroform disappears); the cuprous oxide, formed according to the equation $CHCl_3 + 2CuO + 5KOH = K_2CO_3 + 3H_2O + 3KCl + Cu_2O$, being weighed. One molecule of chloroform corresponds with 2 atoms of copper.

It can also be determined by heating with alcoholic potash in a reflux apparatus on the water-bath; it is then diluted with water, the alcohol distilled off, and the potassium chloride formed (together with potassium formate, *see* preceding page) titrated with a standard silver nitrate solution. *This method serves for the estimation of all alkyl-halogen compounds.*

The price of industrial chloroform is about £8 per 100 kilos; redistilled costs 2*s.* 10*d.* per kilo; the pharmacopœial preparation 2*s.* 2*d.*; puriss. from chloral, 6*s.* 5*d.* to 9*s.* 7*d.*; Pictet's, 12*s.* per kilo, and that of Anschütz 10*d.* per 50 grms. Part of the chloroform consumed in Italy is imported from abroad; in 1906 this amounted to 12,200 kilos; in 1907, 10,100; in 1908, 7000; and in 1909, 9000 kilos of the value £680.

IODOFORM (Tri-iodomethane), CHI_3, was discovered by Serullas in 1822, and its constitution was established by Dumas who, unlike his predecessors, did not overlook the very small proportion of hydrogen (0·25 per cent.) present.

It is formed by heating ethyl alcohol or acetone with iodine and sufficient alkali hydroxide or carbonate to decolorise the iodine (*Lieben's reaction*):

$$C_2H_5OH + 8I + 6KOH = CHI_3 + H{\cdot}COOK + 5KI + 5H_2O.$$

This reaction (separation of yellow crystals and formation of a characteristic odour) is so sensitive that it serves for the detection of minute traces (1 : 2000) of ethyl alcohol or acetone in other liquids (waiting 12 hours for the separation of crystals if the amount of alcohol is small); the same reaction is, however, given by isopropyl alcohol, acetaldehyde (and by almost all compounds containing the group $CH_3{\cdot}CO$), but not by methyl alcohol, ether, or acetic acid.

For the practical preparation of iodoform 32 parts of K_2CO_3 are dissolved in 80 parts of water and 16 parts of alcohol, the mixture being heated to 70° and 32 parts of iodine gradually added. The separated iodoform is filtered off and the iodine of the potassium iodide in the filtrate utilised as follows: 20 parts of HCl are added and 2–3 parts of potassium dichromate, the liquid being then neutralised with K_2CO_3, mixed with a further 32 parts of K_2CO_3, 16 parts of alcohol and 6 parts of iodine. On heating, a second quantity of iodoform separates, and after this or another similar operation the mother-liquor is treated to recover the iodine from the potassium iodide.

It has been proposed to prepare iodoform by treating the metallic acetylides (*see* p. 91) with iodine and caustic soda.

It seems that practical use is now made of the old electrolytic process, using a bath of 6 parts KI, 2 parts soda, 8 vols. alcohol, and 40 of water at 60–65°. The iodine to be used in the reaction is set free at the anode and to avoid the formation of a little iodate with the KOH formed at the cathode the latter is enclosed in parchment paper.

When pure, iodoform crystallises in hexagonal, yellow plates (sp. gr. 2), insoluble in water but soluble in alcohol or ether. It has a penetrating and persistent odour, recalling partly that of saffron and partly that of phenol. It melts at 119°, readily sublimes, and is volatile in steam. On heating with either alcohol or reducing agents, it gives methylene iodide.

It is used in surgery as an important antiseptic, which, however, acts indirectly on bacteria by means of the decomposition products formed from it under the action of the pus of wounds or of the heat of the body.

Owing to its disagreeable odour, it has been to some extent replaced latterly by **Xeroform**, which is a *tribromophenoxide of bismuth*, $C_6H_2Br_3O{\cdot}OH, Bi_2O_2$, obtained by the action of bismuth chloride on sodium tribromophenoxide and forming a tasteless, odourless, yellow powder insoluble in water or alcohol; it is used also as a disinfectant for the intestines, and costs 44*s*. to 48*s*. per kilo, whilst iodoform costs only 24*s*. to 28*s*. a kilo.

TESTS FOR IODOFORM. It should leave no residue on sublimation and should dissolve completely in alcohol or ether. It is estimated by heating about 1 grm. with about 2 grms. of silver nitrate and 25 c.c. of concentrated nitric acid (free from chlorine) in a reflux apparatus so that the liquid does not boil; when the nitrous vapours have disappeared the liquid is diluted with water to 150 c.c. and heated, the silver iodide being collected on a tared filter, dried and weighed: 1·789 grm. AgI corresponds with 1 grm. iodoform.

CARBON TETRACHLORIDE (Tetrachloromethane), CCl_4 (*see* vol. i, p. 378).

POLYCHLORO-DERIVATIVES OF ETHYLENE AND ETHANE.[1] Asymm. HEPTACHLOROPROPANE was prepared in 1910 by Böeseken and Prins from tetrachloroethylene and chloroform in presence of aluminium chloride as catalyst.

[1] Since 1908 (Ger. Pats. 196,324, 204,516, 204,883, &c.), the Chemische Fabrik Griesheim-Elektron of Frankfort, and the Usines électriques de la Lonza of Geneva have placed on the market, as *non-inflammable solvents* for industrial purposes, six chlorinated compounds obtained as colourless liquids by the action of chlorine on acetylene. They are all good solvents for fats, resins, rubber, &c., and can replace advantageously benzene, carbon disulphide, and alcohol, since they are not inflammable and their vapours do not form explosive mixtures with air; even

II. HALOGENATED DERIVATIVES OF UNSATURATED HYDROCARBONS

These are obtained from saturated halogen derivatives by partial elimination of the halogen hydracid: $C_2H_4Br_2 = HBr + C_2H_3Br$. They are formed by incomplete saturation, with halogens or halogen hydracids, of the less saturated hydrocarbons: $C_2H_2 + HBr = C_2H_3Br$ (*see* Table in footnote).

The allyl compounds, C_3H_5X, are formed from allyl alcohol by the action of halogen hydracid or of phosphorus and halogen.

ALLYL CHLORIDE (Chloro-3-propene-1), $CH_2 : CH \cdot CH_2Cl$, the *bromide* and *iodide* having analogous constitutions.

They are related to the natural allyl compounds (garlic oil and mustard oil). Two stereoisomerides are known:

a-chloropropylene, $\begin{array}{c} H—C—Cl \\ \| \\ H—C—CH_3 \end{array}$ and *iso-a-chloropropylene*, $\begin{array}{c} H—C—Cl \\ \| \\ CH_3—C—H \end{array}$

CC. ALCOHOLS

These form an important group of organic compounds containing one or more characteristic hydroxyls, the hydrogen of which has pronounced reactive properties, so that numerous series of other compounds are derived from the alcohols. They have a neutral reaction, although their chemical behaviour is analogous to that of the inorganic bases which always contain the anion OH′. The majority of these alcohols are colourless liquids, but those of high molecular weights are oily, solid, and sometimes of a yellowish colour. The first members of the series are soluble in water, but with increase of molecular weight the solubility decreases and the smell, generally slight, also tends to disappear. They are often found in nature either free or combined with organic acids, in the fats, waxes, fruits, essential oils, &c.

According to the number of hydroxyl groups they contain, they are divided into *mono-*, *di-*, . . . *polyhydric alcohols,* and may belong either to the saturated or to the unsaturated series—already studied in connection with the hydrocarbons—of which they retain the fundamental characters; added to the latter are those characteristic of the alcoholic group, which we shall study generally with the monohydric alcohols.

carbon tetrachloride they have the advantage of not attacking the metal parts of the extraction apparatus, and the loss on extraction varies from 0·3 to 0·8 per cent.; they are, however, dearer than the ordinary solvents and seem to be injurious to health. The properties of these compounds are given in the following Table:

	DICHLORO-ETHYLENE $C_2H_2Cl_2$	TRICHLORO-ETHYLENE C_2HCl_3	TETRA-CHLORO-ETHYLENE C_2Cl_4	TETRA-CHLORO-ETHANE $C_2H_2Cl_4$	PENTA-CHLORO-ETHANE C_2HCl_5	HEXA-CHLORO-ETHANE C_2Cl_6
Common name	*Dieline*	*Treline*	*Etiline*	*Tetraline*	*Pentaline*	—
Specific gravity	1·278	1·471	1·628	1·600	1·685	2
Boiling-point	52°	85°	119°	144°	159°	(185°)
Vapour pressure at 20°	205 mm.	56	17	11	7	3
Specific heat at 18°	0·270	0·233	0·208	0·227	0 207	—
Heat of evaporation	41 cals.	57 8	50	52·8	45	—
Freezing-point	—	−70°	—	− 30°	—	—
Uses and properties	Readily dissolves rubber	Dissolves fats, paraffin, and vaseline better than benzene	Serves well for removing spots	Dissolves resins and varnishes, like turpentine and alcohol and dissolves cellulose acetate for films and artificial silk	Readily dissolves cellulose acetate for artificial silk and cinematograph films	Has an odour like camphor, and serves as an insecticide

I. SATURATED MONOHYDRIC ALCOHOLS

The specific gravity of these is always lower than that of water and up to the C_{16} member they distil unchanged at the ordinary pressure ; beyond that reduced pressure must be employed.

That alcohols always contain a hydroxyl group OH can be shown by the following chemical reactions :

The alcohols can be obtained by the action of silver hydroxide, AG·OH (which certainly contains the group OH), or even of the alkalis or hot water, on halogenated hydrocarbons: $C_nH_{2n+1}I + AgOH = AgI + C_nH_{2n+1}OH$.

With the halogen hydracids the hydroxyl separates from the alcohols in the form of water: $C_nH_{2n+1}OH + HBr = H_2O + C_nH_{2n+1}Br$; and the same happens with oxy-acids, the so-called *esters* being formed: $C_nH_{2n+1}OH + HNO_3 = H_2O + C_nH_{2n+1}NO_3$. Just as sodium and potassium react with water, liberating hydrogen, so do they act on the alcohols, from which only the *typical hydrogen* (hydroxylic), not united directly to carbon, is eliminated: $C_nH_{2n+1}OH + Na = C_nH_{2n+1}ONa$ (*sodium alkoxide*) + H. *Magnesium alkoxides* are also easily obtained. With phosphorus trichloride, however, the hydroxyl group is eliminated :

$$3C_nH_{2n+1}OH + PCl_3 = 3C_nH_{2n+1}Cl = P(OH)_3.$$

On p. 16 the difference in constitution between ethyl alcohol and methyl ether has been demonstrated.

If the hydroxyl group occurs in place of a hydrogen atom in the *methyl* group ($—CH_3$) at the extremity of the hydrocarbon chain, the *primary alcohols* are obtained, all containing the characteristic group $—CH_2·OH$ $\left(i.e.\ —C\begin{smallmatrix}H_2\\OH\end{smallmatrix}\right)$, *e.g.* propyl alcohol, $CH_3·CH_2·CH_2·OH$, and by oxidation of these alcohols are formed first *aldehydes* with the characteristic group $\left(X—C\begin{smallmatrix}O\\H\end{smallmatrix}\right)$, and then *acids* with the characteristic *carboxyl* group $—COOH$ $\left(i.e\ —C\begin{smallmatrix}O\\OH\end{smallmatrix}\right)$. Substitution of a hydroxyl for a hydrogen atom in an intermediate *methylene* group ($= CH_2$) in the saturated hydrocarbon chain yields *secondary alcohols*, which have the characteristic group $>CH·OH$ $\left(i.e.\ >C<\begin{smallmatrix}H\\OH\end{smallmatrix}\right)$ and on oxidation give *ketones* containing the special group $>CO$. Finally the substitution of the hydrogen of a branched hydrocarbon may take place in the *methinic* group ($\equiv CH$), giving *tertiary alcohols* with the characteristic grouping $\equiv C·OH$, the other three valencies of the carbon being united to three carbon atoms. When the secondary alcohols are oxidised they cannot give either acids or ketones with an equal number of carbon atoms, but, if the oxidation is energetic, the chain breaks, and then acids and ketones may be formed, but with less numbers of carbon atoms.

According to B. Neave (1909), primary, secondary, and tertiary alcohols can be distinguished by the *Sabatier and Senderens reaction* (*see* p. 34), by passing the vapours of the alcohol over finely divided copper heated at 300° ; the primary alcohols form hydrogen and aldehydes (recognisable by Schiff's reaction ; *see* section on Aldehydes), the secondary ones give hydrogen and ketones (detectable by semicarbazide hydrochloride solution) and the tertiary alcohols give water and unsaturated hydrocarbons (which decolorise bromine water).

The primary alcohols and the corresponding ethers have the highest boiling-points, the tertiary ones and, in general, those with branched chains showing the lowest boiling-points.

In the group of alcohols the *isomerism* and the number of isomerides are

similar to those of the halogenated derivatives of the hydrocarbons, since the halogen atom is here replaced by a hydroxyl group.

The *names* of the primary alcohols are made from those of the corresponding hydrocarbons (*see* p. 31) with the termination *ol*, and those of the secondary and tertiary alcohols are derived from the names of the hydrocarbons with the longest non-branched chains; or the secondary and tertiary alcohols may be regarded as derivatives of methyl alcohol or *carbinol*, $CH_3\cdot OH$, formed by substitution of the hydrogen atoms of the methyl group. We have, hence, two different, but still equally clear, systems of nomenclature. For example:

(1) *Normal butyl alcohol:* $CH_3\cdot CH_2\cdot \underset{2}{CH_2}\cdot \underset{1}{CH_2}\cdot OH$ = butan-1-ol or n-propylcarbinol.

(2) *Secondary butyl alcohol:* $CH_3\cdot CH_2\cdot \underset{2}{CH(OH)}\cdot \underset{1}{CH_3}$ = butan-2-ol or methylethylcarbinol.

(3) *Isobutyl alcohol.* $\overset{1}{CH_3}\cdot \overset{2}{\underset{\displaystyle |\atop CH_3}{CH}}\cdot \overset{3}{CH_2}\cdot OH$ = 2-methylpropan-3-ol or isopropylcarbinol.

(4) *Tertiary butyl alcohol:* $\overset{1}{CH_3}—\overset{2}{\underset{\displaystyle \diagup\ \diagdown \atop CH_3\quad OH}{C}}—\overset{3}{CH_3}$ = 2-methylpropan-2-ol or trimethylcarbinol.

PROCESSES OF FORMATION OF MONOHYDRIC ALCOHOLS. As well as from the halogen derivatives, the alcohols can usually be obtained by decomposing esters with acids, alkalis, or superheated water. This reaction is termed *saponification* or *hydrolysis*:

$$C_2H_5O\cdot NO_2 + KOH = KNO_3 + C_2H_5\cdot OH.$$

In a general way, the *primary alcohols* are formed by reducing the acids ($C_nH_{2n}O_2$) or aldehydes ($C_nH_{2n}O$) with nascent hydrogen:

$$CH_3\cdot C\begin{matrix}\nearrow O \\ \searrow H\end{matrix} \text{ (acetaldehyde)} + 2H = CH_3\cdot CH_2\cdot OH.$$

Since the acids, in their turn, can be prepared from the alcohols with one carbon atom less, we have at our disposal a general reaction for preparing synthetically any higher alcohol.

The *secondary alcohols* are formed by reducing the ketones, $C_nH_{2n}O$, *e.g.*:

$$\underset{\text{Acetone}}{CH_3\cdot CO\cdot CH_3} + H_2 \quad = \quad \underset{\text{Isopropyl alcohol}}{CH_3\cdot CH(OH)\cdot CH_3}$$

(*see later*, Aldehydes and Ketones).

The *tertiary* alcohols are formed by the *prolonged* action of zinc methyl on acid chlorides, the intermediate compounds thus formed being decomposed with water.

For the *secondary* and *tertiary* alcohols Grignard's reaction may also be employed (*see later*, Alkylmetallic Compounds).

Of more industrial importance, however, is the preparation of some of the more common of these alcohols by the distillation of wood or the fermentation of certain carbohydrates (*see later*).

In addition to the properties of the alcohols given above, namely, their behaviour towards acids, halogens (which oxidise them), chlorides, and oxidising agents in general (which give aldehydes and acids), it may be mentioned that the higher alcohols (primary) are transformed into the corresponding acids by simple heating with soda lime. Traces of primary alcohols are detectable by oxidising with permanganate and sulphuric acid and then testing for aldehyde with a sulphurous acid solution of fuchsine.

PHYSICAL CONSTANTS OF THE MONOHYDRIC ALCOHOLS

Name and Formula	Specific gravity	Melting-point	Boiling-point
1. Methyl alcohol, $CH_3 \cdot OH$	0·812 (0°)	−94°, −98°	66°
2. Ethyl alcohol, $C_2H_5 \cdot OH$	0·806	−112° −117°	78°
3a. Normal propyl alcohol (prim.) $CH_3 \cdot CH_2\, CH_2 \cdot OH$	0·817	−127°	97°
3b. Isopropyl alcohol (sec.) $CH_3 \cdot CH(OH) \cdot CH_3$	0·789 (20°)	—	81°
4a. Normal butyl alcohol (prim.), $C_4H_9 \cdot OH$	0·810	−80°(−122°)	117°
4b. Normal butyl alcohol (sec.), $C_4H_9 \cdot OH$	0·808	—	100°
4c. Isobutyl alcohol, $C_4H_9\, OH$	0·806 (20°)	—	107°
4d. Tertiary butyl alcohol (trimethylcarbinol), $C_4H_9 \cdot OH$	0·786 (20°)	+25°	83°
5a. Normal amyl alcohol (prim.) $CH_3 \cdot [CH_2]_3 \cdot CH_2 \cdot OH$	0·817 (20°)	—	138°
5b. Amyl alcohol of fermentation or isobutylcarbinol, $(CH_3)_2CH \cdot CH_2 \cdot CH_2 \cdot OH$	0·810 (20°)	—	130°
5c. Active amyl alcohol or sec. butylcarbinol, $CH_3\, CH(C_2H_5) \cdot CH_2 \cdot OH$	0·816 (20°)	—	128°
5d. Trimethyl- or tertiary butyl-carbinol, $(CH_3)_3C \cdot CH_2 \cdot OH$	0·812 (20°)	49°	113°
5e. Diethylcarbinol, $C_2H_5 \cdot CH(OH) \cdot C_2H_5$	0·831 (0°)	—	117°
5f. Methylpropylcarbinol, $CH_3 \cdot [CH_2]_2\, CH(OH) \cdot CH_3$	0·824 (0°)	—	119°
5g. Methylisopropylcarbinol, $(CH_3)_2CH \cdot CH(OH) \cdot CH_3$	0·819 (0°)	—	112·5°
5h. Dimethylethylcarbinol, $(CH_3)_2C(OH) \cdot C_2H_5$	0·814 (15°)	−12°	102°
6. Normal hexyl alcohol (prim.), $C_6H_{13}\, OH$	0·833 (0°)	—	157°
7. Normal heptyl alcohol (prim.), $C_7H_{15} \cdot OH$	0·836	—	175°
8. Normal octyl alcohol (prim.), $C_8H_{17}\, OH$	0·839	—	191°
9. Normal nonyl alcohol, $C_9H_{19} \cdot OH$	0·842	−5°	213°
10. Decyl alcohol, $C_{10}H_{21} \cdot OH$	0·839	+7°	231°
11. Undecyl „ $C_{11}H_{23} \cdot OH$	—	+19°	131°(15mm.)
12. Dodecyl „ $C_{12}H_{25} \cdot OH$	0·831	24°	143° „
13. Tridecyl „ $C_{13}H_{27} \cdot OH$	—	30·5°	156° „
14. Tetradecyl alcohol, $C_{14}H_{29} \cdot OH$	0·824	38°	167° „
15. Pentadecyl alcohol, $C_{15}H_{31} \cdot OH$	—	45–46°	—
16. Hexadecyl (cetyl) alcohol, $C_{16}H_{33} \cdot OH$	0·818	50°	190° „
17. Octodecyl alcohol, $C_{18}H_{37} \cdot OH$	0·813	59°	211° „
18. Ceryl „ $C_{26}H_{53} \cdot OH$	—	79°	—
19. Myricyl „ $C_{30}H_{61} \cdot OH$	—	85°	—

By the behaviour of the nitro-compounds (prepared from the corresponding iodides and silver nitrite) and also by the initial velocity and degree of esterification, primary alcohols can be differentiated from the secondary and tertiary ones.

Various primary normal alcohols enter inorganic compounds as alcohol of crystallisation, *e.g.* BaO, $2CH_3 \cdot OH$; $CaCl_2$, $4CH_3 \cdot OH$; KOH, $2C_2H_5 \cdot OH$; $MgCl_2$, $6C_2H_5 \cdot OH$; $CaCl_2$, $4C_2H_5 \cdot OH$, &c.; it is hence evident why calcium chloride cannot be used for drying alcohol, although it serves well in the case of ether.

METHYL ALCOHOL, $CH_3 \cdot OH$ (Methanol or Carbinol)

This is called *wood-spirit,* since it was obtained by Boyle in 1661 from wood-tar, and is to-day prepared in large quantities by distilling wood. Its chemical composition was not determined until 1834 (by Dumas and Peligot).

In nature it occurs in the form of its salicylic ester, in *Gaultheria procumbens* (in Canada) and as butyric ester in the bitter seeds of *Heracleum giganteum.*

PROPERTIES. When pure it is a colourless liquid, b.pt. 66°, with a faint alcoholic smell; it burns with a non-luminous flame, solidifies at very low temperatures and melts at −94°. When 1 kilo is burned, 5310 cals. are developed. It dissolves in all proportions in water, alcohol, ether, or chloroform. Its specific gravity at 15° is 0·7984, and in aqueous solutions the amount of the alcohol present can be determined from the specific gravities.[1]

Like spirits of wine (ethyl alcohol) it is intoxicating, dissolves fats, oils, &c., and when it is anhydrous it dissolves also calcined copper sulphate forming a bluish green solution.

It is more poisonous to the human organism than ethyl alcohol, since it produces fatty degeneration of the liver and undergoes changes quite different from those of ethyl alcohol, passing only in minimal quantities into the urine and being mostly oxidised in the organism.

When heated with soda lime or with oxidising agents it readily yields formaldehyde and formic acid, and sometimes carbon dioxide; when distilled with zinc dust it gives CO and H. With potassium it forms a crystalline alcoholate, $CH_3 \cdot OK, CH_3 \cdot OH$.

INDUSTRIAL PREPARATION. In the laboratory methyl alcohol can be prepared by saponifying methyl chloride or iodide. Industrially, if wood is heated in retorts out of contact with air, after all the water has distilled over, gradual decomposition commences at 150°, and between 150° and 280° acetic acid (about 5 per cent. of the weight of wood), acetone (0·1 to 0·2 per cent.), methyl alcohol (0·5 to 0·8 per cent.), certain ammonia bases, &c., distil over in the form of a reddish brown aqueous liquid of empyreumatic odour, termed *wood-spirit,* and containing about 10 per cent. of acetic acid, 1 to 2 per cent. of methyl alcohol and 0·1 to 0·5 per cent. of acetone. Between 300° and 400° the distillate is mainly black, oily, dense *wood-tar* (about 10 per cent. of the wood), and at the same time gases (about 6·5 per cent.) are developed which are utilised for heating the retorts. At the end of the distillation, *charcoal* (about 18 per cent.) remains in the retorts. If the distillation is rapid, a greater yield of charcoal is obtained, whilst with slow heating more volatile and liquid products are obtained and only 9 to 10 per cent. of charcoal.

As the principal product of the distillation of wood is acetic acid, the description of the apparatus employed in this industry will be left until later.

[1]

Specific gravity at 15·56°	Per cent. by weight of alcohol	Specific gravity at 15·56°	Per cent. by weight of alcohol	Specific gravity at 15·56°	Per cent. by weight of alcohol	Specific gravity at 15·56°	Per cent. by weight of alcohol	Specific gravity at 15·56°	Per cent. by weight of alcohol
0·99729	1	0·96524	22	0·93335	42	0·89358	62	0·84521	82
0·99554	2	0·96238	24	0·92975	44	0·88905	64	0·84001	84
0·99214	4	0·95949	26	0·92610	46	0·88443	66	0·83473	86
0·98893	6	0·95655	28	0·92237	48	0·87970	68	0·82938	88
0·98569	8	0·95355	30	0·91855	50	0·87487	70	0·82396	90
0·98262	10	0·95053	32	0·91465	52	0·87021	72	0·81849	92
0·97962	12	0·94732	34	0·91066	54	0·86535	74	0·81293	94
0·97668	14	0·94399	36	0·90657	56	0·86042	76	0·80731	96
0·97379	16	0·94055	38	0·90239	58	0·85542	78	0·80164	98
0·97039	18	0·93697	40	0·89798	60	0·85035	80	0·79589	100
0·96808	20								

To separate the methyl alcohol from the liquid products of the distillation these are subjected to fractional distillation in copper boilers with a Pistorius rectifier (*see* Ethyl Alcohol), and when the specific gravity of the distillate has increased from 0·9 to 1 all the methyl alcohol (*crude wood-spirit*) has passed over and forms a greenish yellow liquid with a disagreeable odour. To eliminate the majority of the impurities the liquid is mixed with about 2 per cent. of lime, left overnight, and then distilled with the Pistorius rectifying apparatus, the acetic acid remaining fixed by the lime.

The *crude methyl alcohol* thus obtained has a specific gravity of about 0·816 (93 per cent.) and is colourless, but it turns brown on standing in the air and becomes turbid on mixing with water. To purify it, it is diluted with water to the sp. gr. 0·935 (about 40 per cent.), left for several days, and after the superficial tarry layer which collects has been removed it is treated with 2 per cent. of lime and distilled almost completely. The distilled product is mixed with 0·1 to 0·2 per cent. of sulphuric acid and rectified, the concentrated alcohol distilling at 64° to 66°, being collected separately; this is used for many industrial purposes, although it contains a small proportion of acetone. The latter can be removed almost completely by transforming the alcohol into an ester (*e.g.* the oxalate, by treatment with concentrated sulphuric acid and potassium dioxalate), which is easily separated from the impurities; by hydrolysing the ester with KOH, distilling and rectifying, pure methyl alcohol is obtained. The acetone can also be got rid of by combining the alcohol with $CaCl_2$, giving the compound $CaCl_2, 4CH_3 \cdot OH$, which is stable at 100°, so that the acetone can be distilled off at 56° together with the other impurities; the residue is then decomposed with water and the pure methyl alcohol distilled.

To ascertain if the alcohol still contains acetone, 10 c.c. of it are treated with caustic soda and an aqueous solution of iodine in potassium iodide; no turbidity due to iodoform should be formed for some time.[1]

According to Farkas's patent (Ger. Pat. 166,360, 1904) alcohol of 92 to 95 per cent. purity is obtained direct if the vapours from the distillation of wood, while still hot, are passed through hot NaOH solution (15° to 20° Bé) and then into hot fatty acids, the alcoholic condensate being rectified by passing the vapours into milk of lime.

USES AND STATISTICS. Methyl alcohol is used for the manufacture of formaldehyde and various aniline dyes, for the preparation of different varnishes and for the denaturation of spirit (ethyl alcohol).

[1] Tests for Methyl Alcohol When pure it should leave no residue on evaporation, should not have an acid reaction towards litmus, and should not contain ethyl alcohol, which can be detected as follows: a little of the liquid is heated with sulphuric acid, diluted with water and distilled, the distillate being treated with permanganate, then with sulphuric acid, and finally with sodium hydrogen sulphite; if ethyl alcohol is not present this liquid will not give a violet coloration with fuchsine solution. Acetone and ethyl alcohol can also be detected by the iodoform reaction (*Lieben's reaction*: *see below and also* p. 101). Proportions of 2 to 3 per cent. of methyl alcohol can be detected by *Scudder and Riggs's reaction* (1906), which consists in treating 10 c.c. of the liquid at 25° with 5 c.c. of concentrated sulphuric acid and 5 c.c. of saturated permanganate solution, decolorising (after two minutes) with sulphurous acid solution and boiling until all smell of sulphur dioxide or acetaldehyde disappears. This liquid is then tested for formaldehyde by adding a few centigrams of resorcinol to 2 c.c. and pouring 1 c.c of pure concentrated sulphuric acid to the bottom of the liquid; a blue ring, due to the formaldehyde formed from the methyl alcohol, forms at the surface of separation of the two liquids. Denigès (1910) detects as little as 1 per cent. of ethyl alcohol by heating the methyl alcohol with bromine water and testing for the acetaldehyde formed with fuchsine solution decolorised with SO_2 (*see* Aldehydes).

Estimation of the methyl alcohol in the commercial product is effected by the Krell-Krämer method: 30 grms. of phosphorus tri-iodide is placed in a flask furnished with a long reflux condenser, down which is poured, drop by drop, 10 c.c. of the methyl alcohol; after a short time the methyl iodide formed is distilled from a water-bath into a graduated cylinder containing a little water; when the distillation is completed, the condenser is rinsed out with water and the volume of the methyl iodide under the water measured at 15°; 5 c.c. of pure methyl alcohol give 7·19 c.c. of methyl iodide.

The *acetone* is estimated by Krämer's method. in a 50 c.c. graduated cylinder with a ground stopper are placed 10 c.c. of a 2N-caustic-soda solution, then 1 c.c. of the alcohol, and, after shaking, 5 c.c of a 2N-iodine solution. After a short time 10 c.c. of ether free from alcohol are added, the liquid shaken and then allowed to stand; the volume occupied by the ether is read off, an aliquot part of it evaporated to dryness on a tared watch-glass and the iodoform crystals dried in a desiccator and weighed: 394 parts CHI_3 correspond with 58 of acetone.

A good commercial methyl alcohol should contain not more than 0·7 per cent. of acetone and at least 95 per cent. of the alcohol; it should distil within 1°; 5 c.c. of 0·1 per cent. permanganate solution should not be decolorised immediately when treated with 5 c.c. of the alcohol, and 25 c.c. of the alcohol, mixed with 1 c.c. of an acetic acid solution of bromine (1 part Br in 80 parts of 50 per cent. acetic acid) should give a yellow solution.

Detection of Methyl Alcohol in Ethyl Alcohol. To 0·1 c.c. of the alcohol, in a test-tube, are added 5 c.c. of 1 per cent. potassium permanganate solution and 0·2 c.c. (not more) of pure, concentrated sulphuric acid. The liquid is shaken and left at rest for 2 or 3 minutes, 1 c.c. of 8 per cent. oxalic acid solution being then added. The mixture is again shaken and when it has assumed a brownish yellow coloration, 1 c.c. of concentrated sulphuric acid is added, decolorisation then occurring in a few seconds. Five c.c. of *rosaniline bisulphite* are then mixed with the liquid, which is afterwards allowed to stand. With ethyl alcohol alone, an intense greenish to violet coloration is obtained, but this disappears after a few minutes. But if the alcohol contains even as little as 1 per cent. of methyl alcohol, the more or less blue coloration persists for several hours.

In 1902, Germany produced 5000 tons of the pure spirit, of which 1151 tons was exported, and imported 4273 tons of the crude product. In 1910 England imported 448,500 galls. of methyl alcohol and exported 47,290 galls. The United States exported 1,691,000 galls. in 1910 and 2,040,000 (£179,600) in 1911.

Pyroligneous alcohol of 90 per cent. strength (French) is sold at £4 12*s.* per 100 kilos; that of 92 to 93 per cent. strength (English) at £4 17*s.* 6*d.*; and that of 95 to 96 per cent. strength for lacs at £5 1*s.* 6*d.*; the purest methyl alcohol, free from acetone, costs £7 per 100 kilos.

ETHYL ALCOHOL, $C_2H_5 \cdot OH$ (Ethanol, Spirit of Wine)

This is found rarely in nature (as butyric ester in *Pastinaca sativa*) and sometimes as an abnormal product in certain vegetables and animals, whilst it is easily formed by the alteration (fermentation) of various organic vegetable substances (saccharine juices, fruits, &c.). It has hence been known from the most remote times. Aqua vitæ or spirit of wine, obtained by distilling alcoholic beverages, was used as early as the eighth century and gave rise to an industry which acquired great renown in the province of Modena in the fourteenth century. Various European races learnt the use of aqua vitæ from the custom introduced everywhere by the soldiers, who consumed large quantities of it during the wars of the Middle Ages. But very soon the northern peoples, who did not produce aqua vitæ from wine, began to prepare alcohol by suitable transformations of the starch in the cereals abounding in their countries. By the beginning of the nineteenth century alcoholic liquors (exciting and enfeebling the nervous system and the brain) were spread over the whole of the civilised world and produced the terrible social scourge of *alcoholism*, much more disastrous in its material and moral consequences than all the other maladies that afflict humanity (*see later*, Alcoholism). Later, however, alcohol gradually acquired agricultural and industrial importance owing to its increasing practical applications in the arts and industries. Since 1830 Germany has extended the manufacture of potato spirit, and in many districts great agricultural advantages have followed the culture of this vegetable, since the waste products from the distilleries serve as nourishment for large numbers of cattle—a source of great direct and indirect profit owing to the abundance of stable manure, which increases the fertility of the land and hence also the crops.

SYNTHESIS OF ALCOHOL. In the laboratory alcohol can be obtained synthetically by hydrolysing ethylsulphuric acid, prepared from ethylene and concentrated sulphuric acid (Faraday and Hennel, 1828). Alcohol is formed by hydrolysing ethyl chloride, and, since ethyl chloride is prepared from ethane, which, in its turn, can be obtained from acetylene and hydrogen at 500° (or in presence of platinum black), the synthesis of alcohol from acetylene can be effected (Berthelot, 1855). Further, acetylene can be obtained from so-called inorganic substances, from C and H (Berthelot); by decomposing calcium carbonate with an acid, carbon dioxide is obtained, and magnesium, burnt in this gas, gives carbon, which, with lime, gives calcium carbide, and this, with water, acetylene; there is hence a *transformation of mineral substances into organic substances.*

In 1907, Jonas, Desmonts, and Deglotigny (Fr. Pat. 360,180) proposed preparing alcohol by first forming acetylene in mercurous nitrate and then heating the mass to boiling; the precipitate decomposes, regenerating the mercury salt and evolving vapours of acetaldehyde, which are condensed and converted into alcohol by means of sodium amalgam (nascent hydrogen).

PROPERTIES. When pure, it is a colourless liquid with a characteristic odour, sp. gr. 0·7937 at 15°, 0·80625 at 0°; it boils at 78·3° (or at 13° under 21 mm. pressure), and its vapour is stable at 300°; at a very low temperature it gives a glassy mass, which at −135° is converted into another solid mass m.pt. −117° (*enantiotropy*, vol. i, p. 191).

When concentrated (absolute) it is extremely hygroscopic, and it mixes

with water or ether in all proportions. To obtain *absolute alcohol*, *i.e.* absolutely free from water, fractional distillation is not sufficient, since at 78·15° an aqueous alcohol containing 95·57 per cent. of alcohol by weight distils; the higher alcohols also give mixtures with water which boil at lower temperatures than the corresponding alcohols. If benzene is mixed with alcohol, the latter can be obtained pure although a mixture of water and benzene first distils over, then alcohol (at 64·8°), then alcohol and benzene (68·2°) and finally pure alcohol.

Usually absolute alcohol is obtained by distilling the ordinary 90 to 96 per cent. alcohol over calcined potassium carbonate or over anhydrous (*i.e.* calcined) copper sulphate, redistilling over lime and finally over baryta or a little sodium or calcium; or it may be left over powdered aluminium until hydrogen ceases to be evolved. The aldehydes of the alcohol can be separated by boiling with 5 per cent. of caustic soda.

If alcohol contains a little water, it becomes turbid on mixing with benzene, carbon disulphide, or paraffin oil, and turns white, calcined copper sulphate blue, and barium hydroxide is precipitated on addition of baryta, the latter dissolving only in the absolute alcohol.

A mixture of 53·9 vols. of alcohol with 39·8 of water gives 100 vols., the contraction of 3·7 per cent. being due to the formation of a labile compound, $(C_2H_5 \cdot OH)_{18}, H_2O$ (or $2H_2O$, &c.). It is a good solvent for resins, oils, colouring-matters, varnishes, ethereal essences and many other substances, and dissolves sulphur and phosphorus to a slight extent; it coagulates proteins and diffuses through porous membranes more rapidly than water. It dissolves and gelatinises soaps.[1]

It unites with various salts and alkalis as alcohol of crystallisation (KOH, LiCl, $CaCl_2$, $MgCl_2$) (*see* p. 107).

It oxidises easily, giving aldehyde and acetic acid, *e.g.* with potassium dichromate, MnO_2 or even H_2SO_4, or oxygen in presence of platinum, or with micro-organisms if the solution is dilute. With concentrated nitric acid, it gives various oxidation products and with the dilute acid, glycollic acid. Alcoholic solutions of caustic alkalis turn brown, since they are partially resinified by the aldehyde which forms first and which acts as a reducing agent. Chlorine gives acetaldehyde and various intermediate chlorinated products. In a red-hot tube it decomposes, giving hydrogen and many hydrocarbons and acids. With sodium it gives *sodium ethoxide* in the form of a white powder.

Absolute alcohol, which plays an important part in organic syntheses, is poisonous and rapidly produces death when injected into the blood.

The complete combustion of 1 kilo of pure alcohol ($C_2H_5 \cdot OH + 6O = 2CO_2 + 3H_2O$) generates 7193 cals. and 96 per cent. alcohol, about 6750 cals.

Alcohol can be detected even in traces (1 : 2000) by means of *Lieben's iodoform reaction* (*see* pp. 101 and 107). This reaction is also given by acetone, isopropyl alcohol, and the aldehydes; according to Buchner (1905) it is preferable to heat the alcoholic liquid with a little paranitrobenzoyl chloride, which forms crystals of ethyl paranitrobenzoate, $NO_2 \cdot C_6H_4 \cdot CO_2C_2H_5$, m.pt. 57°. In *Rimini's reaction*, the liquid is heated with sulphuric acid, and a dilute solution of potassium dichromate: the green colour of the solution and the odour of acetaldehyde are sufficiently characteristic, but the reaction can be confirmed by distilling a few drops of the liquid and treating the distillate

[1] Solid Alcohol is nothing but a soapy mass formed from about 20 per cent. of water, 20 per cent. of soap (sodium stearate) and 60 per cent. or more of alcohol; it burns like liquid alcohol but leaves a residue.

A richer product can be prepared by heating and stirring 100 parts of 96 per cent. alcohol at 60°, dissolving 1 part of stearine and adding 0·5 part of a 30 per cent. aqueous sodium hydroxide solution—just sufficient to make it redden phenolphthalein. Some use a sodium soap charged with silicate (500 per cent.). A solid alcohol that burns without leaving a residue can be obtained by dissolving 20 to 40 parts of collodion in 100 parts of alcohol; others add, instead, 25 parts of a 25 per cent. solution of cellulose acetate in acetic acid, and shake, the crust of solid alcohol which separates being squeezed out.

with a little sodium nitroprusside and a drop of piperidine, a beautiful blue coloration being obtained if acetaldehyde is present.

The manufacture of alcohol became one of the great chemical industries when a scientific explanation was obtained of the phenomena governing the transformation of starch and sugar. Fermentation, although known from the most ancient times, remained unexplained up to the nineteenth century, and it is solely, or largely, owing to the studies of Caignard de Latour and Schwann, Turpin, Schroeder, Liebig, Pasteur, Nägeli, Cohn, de Bary, and, more recently, Duclaux, Buchner, &c., that the phenomena of *fermentation* are now completely explained and rationally regulated.

In 1836 Caignard de Latour and Schwann found that the fermentation of wine and beer is strictly dependent on the germination of microscopic fungi which multiply in the must or wort. Turpin supposed that these fungi are nourished by the sugar, producing, as the excreta of their vital action, alcohol and carbon dioxide. In 1838 Liebig held that this transformation of sugar is caused by a special intermolecular movement due to substances contained in the ferment itself (microscopic fungus).

Pasteur, in 1872, showed that certain ferments that live at the expense of the oxygen of the air and can decompose sugar into water and carbon dioxide, when they are immersed in saccharine liquids, being no longer able to assimilate oxygen from the air, extract it from the sugar, resolving the molecule of the latter into alcohol and carbon dioxide. Although Nägeli, in 1879, had attempted to reconcile the hypotheses of Liebig and Pasteur, yet up to a few years ago all fermentative phenomena were interpreted on the basis of the ideas enunciated by Pasteur. Progress in the fermentation industry proceeded, *pari passu*, with that of bacteriology.[1]

[1] Bacteriology is the science which studies morphologically and biologically the smallest, unicellular, vegetable organisms which are propagated with immense rapidity by *segmentation*. The cell is formed, as in the other organisms, of an extremely thin *membrane* which permits all the osmotic phenomena (*see* vol i, p. 77), and encloses the *protoplasm* in which no central nucleus is visible, but in which there occur scattered granules (of starch and other substances), fat globules, vacuoles containing cell-sap, and sometimes crystals (*e g.* of sulphur), while in certain bacteria the protoplasm holds various colouring-matters in solution. The temperature most favourable to their vitality varies, according to the species, from 5° to 40°; they live, however, in a latent condition, at very low temperatures, although they do not reproduce, and they usually die at about 70° (excepting the spores, *see below*). As, in general, they do not contain chlorophyll, they are nourished by complex organic substances already elaborated by other organisms and hence soluble or capable of being rendered soluble (sugars, organic ammonium salts, ammonium compounds, &c.); and in this they are clearly differentiated from vegetable organisms and approximate more to the animals. Nutrient matter for bacteria always contains phosphorus, sulphur, potassium, and calcium, and, in certain cases, magnesium and manganese. They live well and reproduce rapidly in meat-broth or nutrient gelatine They tolerate more easily alkaline than acid media and *direct* sunlight kills many species of bacteria, even pathogenic ones. As a result of their vital actions, substances are sometimes formed which kill the bacteria themselves. Different antiseptics have various actions on different bacteria, or else only a specific action on certain of them. The *reproduction* of bacteria takes place ordinarily by *segmentation*, that is, when the cell has reached a certain length a thin wall forms in the middle and divides the cell into two new ones; these divide, in their turn, so that the reproduction of these organisms, which increase in geometrical proportion (1, 2, 4, 8, 16, 32, &c.), proceeds with prodigious rapidity and yields millions of individuals in a few hours. The universal distribution of bacteria is thus easily understood. When the vital conditions are rendered abnormal or difficult for bacteria, in many of them there occurs a contraction of their protoplasm into a more compact mass (at the centre or laterally, according to the species), which forms a separate individual, the *spore*, much more resistant to cold (−180°) and heat (130–140°), and even to antiseptics than the corresponding bacterial cell; the spores can retain life even for some years. Under favourable conditions, the spore breaks its envelope and gives a cell which reproduces by segmentation like the original one. Only certain rare species of bacteria are provided with chlorophyll or other colouring-matters capable of assimilating carbon dioxide under the action of sunlight.

These micro-organisms, termed *bacteria* or *schizomycetes* or microbes, are those which produce putrefaction and infectious diseases (cholera, carbuncles, typhus, tuberculosis, small-pox, diphtheria, &c.); they are classified, according *to their form*, into. (1) Desmobacteria (*bacillus* or vibrio forms like small rods); (2) Sphero bacteria (*cocci* and *micrococci* of spherical shape and termed *diplococci* if united in twos, *staphylococci* if joined in bunches, and *streptococci* if in strings); (3) Spirobacteria (*spirilla* of twisted shape). To give a concrete idea of their forms de Bary described them as analogous to a pencil, a billiard ball, and a corkscrew.

On the basis of their different activities and physiological properties Cohn divided all the species of bacteria into three characteristic groups: (1) *zymogenic*, or those which produce all the non-alcoholic fermentations; (2) *chromogenic*, which produce various colouring-matters (red, violet, yellow, &c.); (3) *pathogenic*, which cause diseases of man and animals. To recognise the latter—given the difficulty of distinguishing them morphologicaly under the microscope, since different species often have the same form and the same species sometimes several forms—they are inoculated into the blood of living rabbits, rats, guinea-pigs, &c., the pathogenic character being deduced from the effects produced in the animals in two or three days, or sometimes even after a few hours.

The lesser diameter (width) of these unicellular bacteria measures a few tenths of a *micron* (1 micron or μ = 0·0001 mm.), and, in rare cases, as much as 1·7 μ; the greater diameter (length) is usually several microns.

If we wish to indicate bacteria in a wider sense of the term, and not to limit them to the *pathogenic* or *saprophytic* (non-pathogenic) but still to those that produce all putrefactions and widen the limits of their dimensions,

During recent times, however, new facts have been discovered which have profoundly shaken the fundamental basis of this theory, according to which no fermentation is possible, except in the presence of certain species of *living* micro-organisms. In reality certain special fermentations are already known which are produced by *enzymes*, *i.e.* substances of complex chemical compositions which do not manifest anything in the nature of living micro-organisms; for example, *diastase* transforms starch into maltose: $2(C_6H_{10}O_5)_x + H_2O = xC_{12}H_{22}O_{11}$.[1]

In 1900 Buchner succeeded in showing, by careful experiment, that some of these fermentations, which in the past could only be induced by the living micro-organisms, could also be effected by using the *extract* of the bacteria obtained by squeezing out, under great pressure, through special unglazed porcelain filters, the extract of the ferment-cells previously ground with quartz-sand. In this way *Saccharomyces cerevisiæ* yields *maltase* (which is an enzyme occurring also in germinating barley or maize and contained in *Saccharomyces octosporus*), which hydrolyses maltose, transforming it into glucose; from beer-yeast is obtained *invertase* (or *invertin*) capable of resolving saccharose or cane-sugar (not directly fermentable) into fructose and glucose (fermentable); fresh yeast cells yield *zymase*, the enzyme capable of effecting the alcoholic fermentation of various six-carbon-atom sugars (glucose, fructose, &c.).

The action of the enzyme cannot be attributed to the still living protoplasm derived from the cells of the ferment, since the protoplasm can easily be killed in a mixture of alcohol and ether, and after this treatment the enzyme retains its activity. The action of ferments is hence due to the enzymes that they are able to produce, rather than to the biological phenomena of the life of the organisms.

To-day numerous enzymes are known which are of great importance in many vital functions of vegetable and animal organisms. It is not certain if the enzymes, with their large and complex molecules, are true proteins, since up to the present they have not been obtained chemically pure; all of them contain nitrogen but, as they are purified more and more, the nitrogen content continually diminishes and to-day it is held by some that the composition of each enzyme approaches that of the substance it transforms; so that diastase would be a substance similar to starch and poor in nitrogen, whilst the enzymes that transform the proteins would be of true protein nature. *Proteolytic* (decomposition of proteins) and fermentative actions only occur

we can logically divide these micro-organisms into two other similar groups of similar beings, namely, the Hyphomycetes (*moulds*) and the Blastomycetes (*ferments*).

The *Hyphomycetes* form groups of branched filaments (*mycelia*), which often subdivide into portions similar to bacteria, but the width of these always exceeds 2μ and often 5μ; they multiply by means of spores and four principal species are distinguished according to the mode of formation of these spores (*conidia*): (1) the *Aspergillus* species which form, at the extremities of the fruit-bearing filaments (*spore-bearing hyphæ*), a swelling in the form of a club covered with series of spores attached by means of intermediate *sterigmata*; (2) the *Mucor* species (or *Mucedineæ*), in which the spore-bearing hyphæ which start from the mass of mycelia carry *sporangia* (species of capsule) in which the spores develop; (3) the *Oidium* species in which the spores are formed directly in the spore-bearing hyphæ without any special organ of fructification; (4) the *Penicillium* species, which is very common and has branched spore-bearing hyphæ in the form of a brush containing series of spores *Aspergillus* and *Oidium* are, however, not separate species but special sporifying forms of *Eurotium* and *Erysiphæ* belonging to the order of *Ascomycetes*.

The most important of these micro-organisms for industrial purposes are the *Blastomycetes*, *i.e.* the ferments or unicellular fungi which usually multiply by gemmation (budding), that is, by excrescences forming on the cells and becoming detached when they have reached a certain size, forming new cells which live independently of the mother-cells; under abnormal conditions, however, the ferments multiply also by means of spores, four nuclei being usually formed inside the cell, these then becoming covered with membranes and dividing the mother-cell into four parts forming four new cells.

The cells of the ferments have often a magnitude greater than 5μ, and the most important for alcoholic fermentation form the family of the *Saccharomycetes* (*see later*).

The extraordinary beneficial influence of the bacteria and ferments in nature (apart from the pathogenic action of certain of them on some of the higher organisms) is manifested in the wonderful destructive activity they exert on the refuse and remains of all the higher organisms, converting the complex substances composing them into continually more simple substances until they give CO_2, H_2O, NH_3, and HNO_3. These are the simplest materials which can be used by vegetable organisms to recommence the life-cycle, since in nature nothing is destroyed or created, but everything is transformed and thus life itself rendered eternal.

[1] *Starch*, which is formed in the green leaves of plants under the action of sunlight and of *chlorophyll*, although an insoluble substance and very resistant to various reagents, emigrates during the night and accumulates in the seeds, roots (tubers), medulla, &c. We can, however, stop the starch in its path, and can explain how it can be transported by the juices into other parts of the plant. In fact, various enzymes occur distributed through plants, and among these is *diastase* or *amylase*, which renders the starch soluble by transforming it into soluble (and hence transportable by the juices) sugar (maltose), to be regenerated by an inverse process—unknown to us—in the form of insoluble starch in other parts of the plant.

between certain limits of temperature (0–65°) and are retarded or prevented by certain poisons (*e.g.* by traces of prussic acid or by metallic salts that act on proteins, like $HgCl_2$, &c., although they are more, and sometimes completely, resistant to the action of antiseptics that kill ferments, such as salicylic acid, boric acid, ether, &c.). The various enzymes produce one or other of the following general reactions: *hydrolysis* (amylases, sucrases), *coagulation* (enzyme of rennet), *decomposition* (zymase of alcoholic fermentation), *oxidation* (laccase oxidises the juice of the lac-tree), &c. Enzymes exhibit different behaviour towards the stereoisomerides of certain hydrolysable and fermentable substances (*see* section on Sugars).[1]

[1] The following are some of the more important enzymes:

Diastase (or *amylase*) occurs abundantly in malt (germinating cereals) but is found also in plants, the pancreas, the saliva, the liver, the bile, the blood, the kidneys, and the mucous membrane of the stomach and of the intestines; it transforms starch into maltose and dextrin.

Maltase transforms maltose into glucose, and is found in malt, in *Saccharomyces cerevisiæ*, and in plants and animals.

Zymase causes alcoholic fermentation of glucose and is contained in yeast and the alcoholic ferments (*Saccharomyces*).

Lactase decomposes milk-sugar.

Melibiase resolves raffinose (or cane-sugar) into molecules of more simple sugars.

Invertase (*sucrase, saccharase,* or *invertin*) decomposes saccharose into glucose and levulose, and is obtained from beer-yeast.

Cytase or Cellase attacks cellulose.

Maltodextrinase ferments maltodextrin.

Dextrinase ferments dextrins.

Peptase governs the important digestive functions of the stomach, and peptonises proteins.

Tryptase is found in the pancreas and contributes to the peptonisation and decomposition of the proteins.

Lipase is also found in the pancreas and renders the fats soluble (hydrolyses them).

Emulsin, contained in bitter almonds, and capable of decomposing amygdalin.

Ptyalin is contained in the saliva and initiates the digestion of starchy foods.

Reductase is capable of effecting reduction phenomena, especially in presence of aldehydes, and is hence also known as *aldehydo-catalase*; it decolorises *Schardinger's reagent* (mixture of methylene blue and formalin). Reductase is widespread in the animal kingdom and occurs in *unboiled milk* (boiled milk is detected by the lack of this enzyme; it does not decompose water or decolorise guaiacol).

The Oxydases form a group of enzymes (*laccase, tyrosinase, œnoxydase, catalase,* &c.) capable of effecting oxidations by fixing the free oxygen of the air and transferring it, in the nascent state, to the substances to be oxidised. They occur widespread in the vegetable kingdom and are also found in the animal kingdom, and their oxidising action is comparable to that of platinum black (catalyst) In fact the *catalase* found in the blood is capable of decomposing H_2O_2, giving nascent oxygen and water (Loew, 1901). It is now found that the oxydases are formed of mixtures of *oxygenase* and *peroxydase*. Euler and Bolin (1909) obtained a laccase of the *Medicago* type in a chemically pure state, and found it to be composed of calcium salts and a small amount of iron salts of mono-, di-, and tri-basic hydroxy-acids, especially citric, malic, mesoxalic, and glycollic acids.

Peroxydases and Oxygenases. Schonbein (1856) had observed that certain vegetable and animal organisms contain substances analogous to ferments and capable of *decomposing* hydrogen peroxide catalytically with liberation of oxygen, and also of accelerating catalytically this decomposition (*i.e.*, the oxidising action) in the same way that ferrous sulphate does Loew (1901) showed that the first action is due to a special enzyme, *catalase* (*oxygenase*). Linossier, in 1898, succeeded in separating from pus an enzyme free from oxydase (oxygenase), yet capable of *accelerating* but not of initiating the decomposition of hydrogen peroxide; this he called *peroxydase*. The oxydases and peroxydases often occur together and they may be separated by heating the mixture to 70°, the oxydase being thus killed, or, as was proposed by Aso of Tokio (1902), by dissolving the peroxydase in alcohol which does not dissolve the oxydase, or by poisoning the latter with sodium fluoride or fluosilicate. There are also several plants that contain only peroxydases, among them pumpkins and horse-radish roots (Bach and Chodat, 1903, 1906).

The peroxydases are nitrogenous but non-protein substances, and, when heated with NaOH give NH_3; they always contain about 6 per cent. of ash, 0·8 to 1·4 per cent. being aluminium and 0·2 to 0·6 per cent. manganese. The peroxydases dialyse, whilst the oxygenases do not. The specific action of the peroxydases consists in *activating* in a remarkable manner the oxidising action of H_2O_2 on organic substances, *e.g.* gallic acid, pyrogallol, &c ; they activate also the action of the peroxides that form in organic substances by the action of the oxygen of the air (*e.g.* ethereal oils, turpentine, &c.).

In 1897 Bertrand introduced the following hypothesis to explain the action of the oxydases: the latter are regarded as hydrolysable manganous protein compounds, in which the manganese, in the manganous condition, is the transmitter of oxygen from the air to the oxidisable substance; the manganese dioxide formed would then be again reduced by the protein acid radical, the original manganous protein compound being regenerated. Bach and Chodat have, however, found manganese in the peroxydases, although these are not direct oxidising agents.

The peroxydases have no oxidising action, unless a peroxide is present. They do not turn fresh guaiacol tincture blue, but after some hours this change does occur, the tincture having formed peroxide, which can be detected by starch and potassium iodide solution. Whilst the peroxydases accelerate the decomposition of very dilute H_2O_2, this kills them if concentrated. In 1908 J. Wolff obtained the reactions of the peroxydases by traces of ferrous sulphate or copper sulphate. The oxidising action of the oxygenases (which have, however, not yet been obtained free from peroxydases, although the latter are known free from oxygenases) is only weak and is strongly activated by addition of peroxydase. On the other hand, it seems established that there are two species of peroxydases existing, the one activating strongly the oxygenases and feebly the decomposition of H_2O_2, and the other behaving in the opposite way. The character of the oxydases themselves is indicated by the specific action of one or the other species of peroxydase. Indeed, Bertrand had in 1896 extracted from certain plants, *e.g.* young potato tubers) an oxydase which differed from all others in not oxidising phenols or the aromatic amines, whilst it oxidised and blackened tyrosine, which is not altered by the ordinary oxydases or even by the presence of H_2O_2 alone. Bach (1906) succeeded in separating the specific peroxydase from tyrosinase and in showing that this peroxydase

But still more interesting is the fact that during an ordinary fermentation the amount of sugar fermented does not depend closely on the quantity of living ferment or enzyme; thus large quantities of sugar can be decomposed by small quantities of ferment or enzyme.

The action of the enzymes and of the ferments may be logically compared with that of the *inorganic catalysts* (vol. i, p. 67), which only produce an enormous increase in the velocity of reaction, in our case, of the decomposition of sugar. And that these *organic catalysts* have an action really similar to that of the inorganic catalysts can be shown by certain other interesting facts.

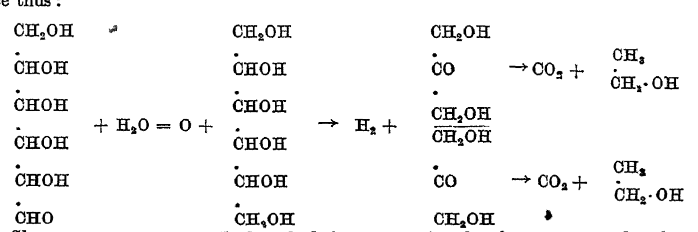
Some years ago Duclaux succeeded in producing alcoholic fermentation by dilute alkali; Traube in 1899 transformed sugar into alcohol by means of finely divided platinum alone at 160°; while Schade in 1906 converted an alkaline solution of glucose, in absence of enzyme, quantitatively into acetaldehyde and formic acid ($C_6H_{12}O_6 = 2C_2H_4O + 2CH_2O_2$), and these products, under the catalytic influence of *rhodium*, are transformed quantitatively into CO_2 and alcohol (perhaps the formic acid first gives CO_2 and H_2, the latter, in the nascent state, reducing the aldehyde to alcohol).[1]

Further, as in chemical equilibria (vol. i, p. 62), the action of catalysts in reversible reactions is regulated by conditions of temperature and of concentration different from those met with in the case of enzymes: indeed, when diastase has converted a certain quantity (dependent on the temperature) of starch into maltose, the hydrolytic change is arrested (*i.e.* equilibrium is reached in the reversible reaction: starch $\leftrightarrows$ maltose); but if part of the maltose is fermented into alcohol and CO_2, the equilibrium is disturbed and the diastase hydrolyses a further quantity of starch. Also at temperatures above 55°, diastase forms dextrin in preference to maltose. An analogous phenomenon is observed in the hydrolysis of *amygdalin* by emulsin. It has already been mentioned that maltase transforms maltose first into glucose, but when a certain proportion between these two products is reached, the hydrolysis ceases owing to equilibrium being attained: $C_{12}H_{22}O_{11} + H_2O \leftrightarrows 2C_6H_{12}O_6$, and the transformation proceeds only when the glucose is removed by alcoholic fermentation; Emmerling has realised the inverse reaction by displacing the equilibrium by addition of glucose (in which case isomaltose is produced).

is only capable of causing the oxidation of tyrosine when mixed with the corresponding oxygenase or in presence of H_2O_2 alone. Hence the action of tyrosinase is due to the specific action of its peroxydase. Bach holds further that in the phenomena of respiration of organisms, oxidation due to oxydases plays no part, since this leads to true condensations, to syntheses of more complex products; for respiratory phenomena there should exist enzymes of a type not yet known and capable of decomposing and oxidising there serve materials of the organism (fats, carbohydrates, &c., which are not oxidised by oxydases).

At the present day the catalytic action of the enzymes is explained as due to small quantities of metal which they contain; thus the important action of the hæmoglobin of the blood (which fixes the oxygen in the lungs in a labile condition and transports it to all parts of the organism) appears to be due to the small quantities of iron present, this inducing the decomposition of the food materials; thus the synthetic action of the peroxydases is perhaps due to the manganese they contain (*see above*), just as the important synthetic functions of chlorophyll, according to Willstatter's recent work, appears to be owing to the magnesium present in it. Recently (1910) Bach has, however, succeeded in preparing very active oxydases and peroxydases free from iron and manganese, so that the true explanation of the activity of these enzymes remains to be discovered.

[1] Buchner and Meisenheimer (1909) explain the action of ferments, from the chemical point of view, by the addition of a molecule of water to the sugar and abstraction of an atom of oxygen by the ferment, so that there results, as an unstable intermediate product, a dihydric alcohol, which, in its turn, is immediately decomposed into H_2 and 2 mols. of dihydroxyacetone; the last product is able to decompose into CO_2 and alcohol, while the hydrogen continues to transform fresh quantities of sugar into the dihydric alcohol, and so on. Boysen-Jensen (1909) finds that the reactions for dihydroxyacetone are given by fermentations; the decomposition would hence take place thus:



Glucose — Dihydric alcohol — 2 mols. of Dihydroxyacetone — 2 mols. of Alcohol

Also in the action of maltase on amygdalin, Emmerling succeeded in producing the reverse reaction, and at the St. Louis Exhibition in 1904 he showed a fine specimen of amygdalin prepared synthetically by an enzymic process.[1]

So that with one and the same enzyme, analytic and synthetic processes can be effected. Cremer obtained *glycogen* $(C_6H_{10}O_5)_y$ from levulose by means of an extract of yeast, and Hanriot, Kastle, and Loewenhart prepared monobutyrin and butyl acetate synthetically by means of *lipase*. The enzymes also effect the so-called *asymmetric syntheses, i.e.* they give *optically active* compounds containing asymmetric carbon (1908).

Also interesting is the fact that a single ferment may contain various enzymes; thus, from *Saccharomyces cerevisiæ*, maltase and invertase can be extracted easily and also zymase, though with more difficulty.

These recent discoveries on the reversibility of the reactions effected by enzymes are of great importance, as it was at first thought that enzymes or ferments in general were capable of causing only decompositions and not synthetical reactions, whereas their analogy with inorganic ferments is now complete. But the discoveries are all the more remarkable, since the same phenomenon of vitality—in the single cell as in more complex organisms—can be reduced to an enzymic phenomenon; that is to say, the exchange of material in the organism (decomposition, recomposition, growth) takes place by means of these organic catalysts, which cause the decomposition of food, preparing various complex materials which form the organism itself, and at the same time generating the energy manifested in the *vitality*, enzymic phenomena being always exothermic. This hypothesis can, with advantage, be substituted for the too abstract *biogen*[2] hypothesis, to explain vital phenomena.

[1] $C_6H_5\cdot CH(CN)\cdot C_6H_{11}O_6 + C_6H_{12}O_6 \rightleftarrows C_{20}H_{27}NO_{11} + H_2O$
Glucoside of phenylglycollic nitrile; Maltase; Amygdalin

or, more completely:

$2C_6H_{12}O_6 + HCN + C_6H_5\cdot CHO \rightleftarrows 2H_2O + C_{20}H_{27}NO_{11}$
Glucose; Hydrocyanic acid; Benzaldehyde

[2] **Hypotheses of Biogen, Toxins, and Genesis of Life.** The physical and physiological basis of life resides especially in the *protoplasm*, the semi-fluid, almost always colourless, refractive substance—insoluble in water—which everywhere constitutes the essential part of the cell. Protoplasm is formed principally from protein substances, whilst it is thought that the fats and carbohydrates are not *active* components. To the protoplasm is attributed the fundamental property of vitality, *i.e.* the exchange of material, but it is not known how its components—the proteins—can have such properties or in what physico-chemical aggregation of the proteins (the plastidules and bionomads are regarded as morphological components or units of protoplasm) they have their origin.

In animals one of the principal functions of the blood is that of supplying the respiratory needs of the tissues in virtue of the *hæmoglobin* contained in the blood of vertebrates [besides *fibrinogen, serum-albumin*, and *paraglobulin*; whilst with the invertebrates there are *echinochrom, chlorocruorin, hæmoerythrin, hæmocyanin* (containing copper), and *pinnoglobin* (containing manganese), which have the same functions as hæmoglobin]; it is formed of a protein substance united with a ferruginous compound, which takes up oxygen at the respiratory surfaces of the organism (skin, bronchi, and lungs), and brings it into close contact with the tissues.

The vital processes of the organism being due to the exchange of material in the cells full of protoplasm, the *biogenic hypothesis* assumes that this is brought about by a very complex, labile compound, which, by being continually decomposed and reconstituted, maintains the interchange uninterruptedly. By many this compound is called *living albumin*, but Max Verworn (1895 and 1902) regards this as an unsuitable name and does not think it has been shown to be a true albuminoid, although it is a nitrogenous substance; there are possibly several substances in a state of labile combination and these he calls *molecules of biogen*.

It has been observed that in organisms, as in parts of them, vitality ceases when oxygen is eliminated, many of them subsequently (the frog even after twenty-five hours) recovering it in presence of oxygen. From this arise two hypotheses: (1) the molecule of biogen becomes labile, and hence gives rise to decompositions and recompositions, that is, to the vital process—since it unites transitorily with oxygen; (2) oxygen serves only to oxidise or eliminate the decomposition products of the biogen (admittedly labile), and when there is no oxygen, these products are not eliminated, so that the decomposition and recomposition of the biogen are arrested. By experiments on the frog Max Verworn has shown that the former hypothesis is the more probable.

Since, in the vital process, under the action of oxygen, it is especially the carbon dioxide that is eliminated, often along with lactic acid, water, &c., whilst the elimination of nitrogenous substances does not increase, it may be assumed that biogen is constituted of a benzene nucleus with lateral chains of carbohydrate and aldehydic character and with an oxygen-carrying nitrogenous group which fixes the oxygen of the air (just as NO gives NO_2 in the lead-chambers of sulphuric acid works) and gives it up to the lateral chain, which is oxidised (Ehrlich's side-chain hypothesis, 1882–1902) to CO_2, lactic acid, H_2O, &c., these being eliminated; the nitrogenous group, thus reduced, remains united with the benzene group, which, with new food, forms the biogen molecule, this

In order to ascertain if a given action is due to enzymes or to organised ferments, the liquid is passed under pressure through a Chamberland porous porcelain filter, which retains the ferment cells, but not the enzymes; the

being again decomposed by oxygen and so on The digested food-materials carry, with the blood, new materials to the regeneration of biogen (without food, death ensues), the oxygen then effecting the changes described above. The seat of the biogen lies in the liquid protoplasm of the cell (not in its nucleus), into which oxygen enters in the state of labile combinations not yet defined but capable of giving it up when needed: these compounds are more stable in the cold than in the hot and are those that carry on the vitality during prolonged fasts. These reserve materials are probably formed by the decomposition of the food by means of intracellular enzymes, which form the connecting-link between the living substance (biogen) and the non-living (foods), transforming the latter into the former.

The biogen hypothesis is opposed by that of the enzymes as factors of the vital process and, given the varied nature of the phenomena and of the chemical transformations occurring in the living organism, and the variety of the numerous chemical groups forming a protein molecule, it is perhaps imprudent to refer all these phenomena to a single compound, biogen, when we already know different enzymes which certainly effect well-investigated, definite reactions. From the action of different enzymes on the protein complex forming the protoplasm of the cell, there results the many-sided phenomenon of vitality. And in certain cases it is possible to go still further, as it must be admitted that many synthetic and analytic phenomena of organic substances (e g. the fermentation of sugar) take place even without protoplasm, by the direct action of the enzyme alone (*see* p. 111).

Further, by simple catalytic actions, it is now possible to effect artificial fertilisation (*artificial parthenogenesis*); for example, by treating unfertilised eggs of the sea-urchin with solutions of various chlorides, best of all, magnesium chloride, Loeb (1899 and 1900) obtained living larvæ; Giard (1904) studied the artificial parthenogenesis of the star-fish (*Asteria rubens*); Tichomiroff (1886 and 1902) and, better, Quajat at Padua (1905) obtained partial artificial parthenogenesis of the virgin eggs of the silk-worm.

Most interesting of all are the investigations on *sero-therapy* which have led to the most unexpected results when, instead of the observations being limited to the bacteria, the poisonous or beneficial substances which they elaborate or secrete have been considered. These *toxins* or *antitoxins* secreted by bacteria or formed in animal organisms also appear to be enzymes, exhibiting, however, their activity in phenomena of a different and more complex nature

In the last few years (1902–1907) Arrhenius, in conjunction first with the head of the German school, Ehrlich, and later with that of the Danish school, Madsen, has devoted himself to the interpretation of *sero-therapy*, making effectual use of all the modern laws of physical chemistry. He has succeeded in following and controlling the formation and action of toxins and antitoxins in the animal organism by empirical mathematical formulæ, calculated beforehand from the results of previous experiments; and it is not improbable that the time will soon arrive when from these empirical formulæ, suitably co-ordinated, rational formulæ will be derived leading to new and important natural laws, from which general pathology will obtain great principles rendering it possible for man and other animals to be immunised against the attacks of pathogenic bacteria. Then, and only then, will man have triumphed over the microbe.

By injecting more or less poisonous substances (*toxins*) into the animal organisms, the so-called anti-bodies (*antitoxins*) are formed in the blood, but their formation is probably incomplete in consequence of the laws of chemical equilibria discovered by Guldberg and Waage (vol. i, p. 62).

The corresponding antitoxins are known for only a few poisons. Those of *solanine* and *saponin* (1901) and of *morphine* (*antimorphine*) (1903) have been sought for in vain by inoculating guinea-pigs and rabbits, so that these three poisons are not to be regarded as toxins. From castor-oil seeds *ricin* has been extracted—a toxin for which the corresponding *antiricin* is known; also, seeds of *Abrus præcatorius* and *Robinia pseudacacia* yield the poisons *abrin* and *robin*, for which the corresponding antitoxins have been obtained. Animals also produce anti-bodies of non-poisonous substances, thus, if any cells whatsoever are injected into the blood, anti-bodies are more or less rapidly produced which have a special destructive action on these cells. Also by injecting *rennet* (which coagulates milk) an *antirennet* is obtained which is able to prevent the coagulating action of the rennet.

From pathogenic bacteria are obtained anti-bodies (by inoculation) to certain proteolytic enzymes: in 1893 Hildebrandt found an anti-body to *emulsin* and Gessard (1901) prepared an anti-body to *tyrosinase* (*see above*); from the serum of a goose inoculated with pepsin, H. Sachs (1902) obtained an *antipepsin*; A. Schütze (1904) obtained *antilactase* by making subcutaneous and intermuscular inoculations with the lactase of *kephir* (*which see*), and similarly were prepared anti-bodies to *cynarase*, *zymase*, *urease*, and the fibrin and pancreatic ferments.

It is difficult to establish a limit or any essential difference between enzymes or ferments and toxins, and the preparation of anti-bodies to all these active substances is, perhaps, only a matter of time. The anti-bodies are divided into two classes, according as they are obtained by inoculation of homogeneous solutions (toxins) or of emulsions of bacteria or cells (red blood corpuscles), &c. The anti-body formed by the inoculation of a homogeneous solution combines with the toxin of the latter, forming an innocuous substance, which is called an *antitoxin* if soluble or a *precipitin* if insoluble. The injection of bacteria sometimes leads to the formation of anti-bodies capable of *dissolving* the bacteria themselves (from which they are derived) and then these anti-bodies are termed *lysins* (*bacteriolysins*). There may also be formed anti-bodies which agglutinate the inoculated cells, *i.e. agglutinins*, but this depends on the presence of salts. The cholesterin and lecithin of the organism often form part of the toxin or antitoxin. Cholesterin, for example, acts as an antitoxin to *tetanolysin* and other lysins. According to Metchnikoff it is the *leucocytes* (white corpuscles) which produce the antitoxins, but this has not been rigorously proved, although Wright has shown that certain anti-bodies (*opsonins*) exhibit their activity against bacteria only in presence of leucocytes.

That the action between *toxins* and *antitoxins* resembles chemical neutralisation was assumed at the time of the discovery of the first diphtheritic antitoxin by Behring and Kitasato in 1890, and was supported by the German school with Ehrlich at its head. From 1893, however, the French school (Roux, Vaillard, Metchnikoff, and also Buchner) held that the antitoxins exert a physiological action, *exciting*, as it were, the organic tissues to resist the attacks of these poisons (toxins). When, however, Ehrlich showed that the agglutinating action of *ricin* on the red blood corpuscles (suspended in physiological serum, that is, in 0·9 per cent. NaCl solution) could be annulled by simply adding *antiricin*, and because he showed that the neutralisation of the action of a given quantity of toxin required the presence of a proportionate amount of antitoxin, most scientific men abandoned the physiological hypothesis. Ehrlich's more recent studies on the action of two arsenical compounds on the toxins have led to the cure of *sleeping-sickness* and probably to that of *syphilis* (by means of the product 606). In suitable conditions of temperature, &c., the original toxins can be regenerated from the antitoxins by a reversible process (Reversible Reactions, vol. i, p. 63); this was shown by Morgenroth (1905) by dissociating

filtered liquid is then examined to ascertain if it still produces the enzymic action. Or the liquid may be mixed with chloroform, which arrests all cellular life, but does not act on the enzymes.

A liquid containing an enzyme is coloured blue by the addition of an alcoholic solution of guaiacum resin, previously mixed with a drop of hydrogen peroxide.

The enzymes are, as a rule, destroyed by boiling.

INDUSTRIAL PREPARATION OF ALCOHOL. As already mentioned, the prime materials are saccharine or starchy substances; the latter, by the action of enzymes (diastase and maltase) are transformed into maltose and glucose, and then by the action of the zymase contained in yeast-cells (species *Saccharomyces*, *see* pp. 111 and 121) the glucose is transformed, to the extent of 95 per cent., into alcohol and CO_2, with evolution of heat.

The treatment of the starchy materials is carried out as follows: the *starch* is obtained from various prime economic materials, namely, *maize* (especially in Italy, Hungary, and America), *potatoes* (Germany, France, England, and Russia; attempts to introduce the potato industry into Italy have as yet come to nothing); *cereals* (Russia and England); *rice* (England, Japan, China, Italy).

There are two practical processes: (1) the action of dilute mineral acids in the hot, and (2) the action of certain hydrolytic enzymes (like *diastase* contained in *malt*).

(1) *Transformation of starch by dilute acids.* In this transformation, starch yields glucose almost quantitatively: $(C_6H_{10}O_5)_n$ (starch) $+ nH_2O = nC_6H_{12}O_6$, and we shall deal more in detail with this process later on, in the section on Glucose. At present only the second process will be considered.

(2) *Transformation of starch by means of enzymes.* Of the enzymes, that which is of the most service industrially, is *diastase.* It is formed more especially during the early stages of the germination of cereals (maize, barley, &c.), and this germinated grain forms *malt* which is most favoured by a temperature of 45–55° in its transformation of starch into dextrins (amylodextrin, erythrodextrin, achroödextrin, $(C_{12}H_{20}O_{10})_x$) and into maltose and isomaltose, $C_{12}H_{22}O_{11}$.

As has been already mentioned (p. 113), this reaction is regulated by the laws of chemical equilibria, and depends especially on the temperature:

the antitoxin with a little HCl and destroying the anti-body at 100°. So that validity can no longer be ascribed to the hypothesis of Behring (1890), Nernst (1904), and Biltz, Much, and Siebert (1905), according to which the toxins are absorbed by the colloidal antitoxins and then *destroyed.*

The toxins and antitoxins, although colloidal substances, diffuse easily and give osmotic pressures according to van 't Hoff's law.

Toxins diffuse through water and gelatine *much* more rapidly than antitoxins, so that a mixture of the two bodies can be separated into its components. The difference in the rapidity of diffusion depends on the molecular magnitudes (according to E. W. Reid, hæmoglobin has a molecular weight of 48,000). The molecular weights of the antitoxins would be 10 to 100 times as great as those of the toxins.

The velocity of reaction of the different toxins does not depend, as Morgenroth supposed, on catalytic actions, but, as Arrhenius and Madsen showed, on the temperature, and is regulated by a law deduced from thermodynamical considerations based on van 't Hoff's laws of solutions.

A number of other factors of the vitality of the organism—digestion of food, assimilation of carbon dioxide by plants, development of the egg, production of alcohol during the fermentation of sugar, &c.—are due to enzymes or toxins and antitoxins, whose actions are regulated by the laws of chemical equilibria and of the velocity of reaction, and are perhaps not disconnected from catalytic phenomena or from reactions similar to or identical with those assumed by the biogen and side-chain hypotheses.

Further, the recent studies of O Lehmann and of S. Leduc (1896) on Liquid Crystals, according to which, under certain conditions, solutions of substances can assume the form of crystals or of cells that grow, multiply, and die, like actual organisms (*see* vol. i, p. 112), furnish a probable explanation of the transition from organic substances to organised bodies. Thus, after what has been stated above, the entire cycle of the genesis of life can be comprehended, from the transformation of inorganic substances into organic (*see* p. 108) and of these into organised (or living), by hypotheses based on scientific facts. It still remains, however, to explain the origin of the inorganic world, terrestrial and extra-terrestrial, the answer of science being that, in accordance with Lavoisier's law, nothing is created and nothing destroyed, so that the inorganic world has always existed and is eternal, and eternal also is its continuous evolution. This is the actual limit of human knowledge, which, in its imperfection, cannot explain the infinite and the eternal. And no metaphysical philosophy has succeeded in obtaining a final clue to this secret of eternity, since it is not a plausible or even rational explanation to refer the eternity of the inorganic world to a hypothetical, abstract, supernatural being who created everything from nothing, in contradiction to the fundamental laws of positive science, the first of all of these being those of the conservation of mass and of energy.

between 45° and 50° maltose is preferably formed, and at about 60°, dextrin.

We have already noticed how maltose is transformed into glucose by means of *maltase*, and how the chemical equilibrium is displaced, by gradually transforming the glucose into alcohol by fermentation.

Of the various malts used industrially, that of barley is the most active, then follow wheat and rye, and, finally, maize; the last named is one-third less active than that of barley, but owing to its low price has practical advantages, and in Italy is the one most commonly used.

In describing the industry of brewing, we shall deal in detail with the practical manufacture of malt, and we would refer the reader to that section for a description of the preparation of maize malt, which does not differ from that of barley malt.

As regards the use of chlorine dioxide to increase the germinative power of maize, as proposed by Effront, *see* vol. i, p. 171.

The starchy matters forming the starting materials of the alcohol industry (cereals, potatoes, &c.) cannot be subjected to the action of diastase unless their starch is first transformed into a semi-solution (starch-paste) by treating with water or steam at a high temperature; the starch-granules swell and then burst and readily assimilate water (potato starch at 65°, maize starch at 75°, barley starch at 80°). The materials are hence first steeped and ground, and then extracted with hot water, to be subjected subsequently to saccharification with malt and finally to alcoholic fermentation.

The following Table gives the amounts of starchy and extractive matters per 100 kilos of various materials, together with the theoretical yields of alcohol:

	Starchy and extractive matters	Alcohol
Wheat	65–68 kilos	32–44 kilos
Maize	62–67 „	31–33 „
Barley	63–65 „	30–32 „
Rye	66–69 „	34–35 „
Rice	78–82 „	39–43 „
Durra	61–64 „	30–32 „
Green potatoes	18–20 „	10–12 „
Dry potatoes	68–70 „	34–35 „

In washed potatoes the starch is calculated from their specific gravity (vol. i, pp. 72 and 107).[1]

In cereals and potatoes the content of starch can be determined as follows: 200 grms. of potatoes (75 grms. of ground cereal) are heated in a flask with 600 c.c. of water and 10 c.c. of hydrochloric acid (sp. gr. 1·2 ≡ 4·7 grms. HCl) for ten hours at 90°, the volume made up to 1 litre and 3·5 grms. of HCl neutralised with caustic soda (leaving 1 grm. free); the whole is poured into a larger flask, a few grammes of beer-yeast being added and the flask kept at 25° for 2 or 3 days until the fermentation is over, when half of the

[1]

Specific gravity of potatoes	Per cent. of starch	Specific gravity of potatoes	Per cent. of starch	Specific gravity of potatoes	Per cent. of starch	Specific gravity of potatoes	Per cent. of starch
1·070	11·5	1·088	15 6	1·106	19 4	1 125	23 5
1·072	11·9	1·090	16 0	1·108	19 9	1·127	24·0
1·074	12·5	1·092	16 4	1·110	20 3	1·129	24·5
1·077	13·1	1·094	16 9	1·113	20·9	1·134	25·5
1·079	13·7	1·097	17·5	1 115	21·4	1·139	26·5
1·081	14·1	1·099	17 9	1·118	22·0	1·144	27·6
1·083	14·5	1 101	18 4	1·120	22·5	1·149	28·7
1·085	14·9	1·103	18·8	1·122	22·9	1·150	28·9

(To 15 per cent. of starch corresponds 20·8 per cent. of dry matter in the potato; to 20 per cent. of starch 25 8 per cent. of dry matter; and to 25 per cent. of starch 30 8 per cent. of dry matter).

liquid is distilled and the alcohol estimated in the distillate by means of the specific gravity. 100 kilos of starch yield practically 63·5 litres of alcohol.[1]

The fresh potatoes are washed free from stones and earth in an Eckert mechanical washer (Fig. 103), passing first into a rotating sieve, *E*, which removes the stones and, by means of the blades, *F*, carries the potatoes into the tank, *A*, through which water flows and in which they are stirred by the vanes, *C*, fixed to a rotating axis; the latter is inclined in such a way that the potatoes are gradually forced to the far end of the tank where a rotating disc, furnished with perforated blades, collects them and removes them from the tank. An elevator raises them to the opening of a Pauksch's improved form of the conical Henze autoclave (Fig. 104), which is made of sheet-iron, has a volume of 2500–3000 litres, and takes about 1500–3000 kilos of potatoes; in this they are treated for an hour or more with steam at 2·5 to 3·5 atmos. pressure. Such an apparatus can also be used for treating maize and other cereals, and gives a much denser wort than was previously obtained when steam at 100° was used; in addition, it effects a better dissolution of the starch, and is of advantage to manufacturers in countries where the alcohol tax is based on the volume of wort fermented (or of the fermenting vats). The steam is passed in at the top by the tube *b*, and is distributed uniformly over the interior by means of a perforated pipe (shown dotted at *c*), the tap, *g*, at the bottom being left open to discharge the condensed water. When the whole mass is hot, steam begins to issue from this tap and drives out all the air. The tap is then shut, and the pressure, shown by the manometer, *e*, soon rises to 3 atmos. After about 45 minutes at this pressure (temperature 135°), the conversion is complete. With damaged or frozen potatoes, the steam is allowed to issue for an hour from the tap, *g*, before raising the pressure, and steam is then passed in by the pipe *b′* as well. A pressure higher than 3 atmos. turns the mass brown, owing to the caramelisation of the maltose. To discharge the apparatus, the pressure is maintained at its maximum and connection made with the discharge pipe, *i*, by opening the valve, *h*. At the bottom of the cone, just above *k* is a horizontal disc of cutting grids, through which the whole of the mass is forced by the steam-pressure and thus converted into a paste; the pipe *i* carries

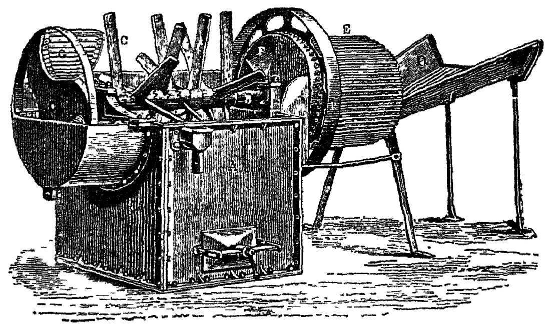


FIG. 103.

[1] Witte (1904) gives the following improved modification of the Baumert and Bode method for estimating the starch in cereals: 1–2 grms. of the meal, sieved and mixed to a paste with water, are heated with 60–70 c.c. of water under 4 atmos. pressure (145°) in a Lintner bottle or other vessel for two hours—in an oil-bath. After being allowed to cool partially, the whole is introduced into a flask and boiled for 10 minutes with a few grains of zinc. When cool, the liquid is made up to a volume of 500 c.c. and filtered through a thin layer of asbestos. To 50 c.c. of the filtrate are added 5 c.c. of 10 per cent. caustic soda solution, about 1 grm. of shredded asbestos and 100 c.c. of 96 per cent. alcohol; the whole is well shaken and then allowed to settle, when the liquid is decanted through an asbestos filter-tube (Allihn); the deposit is also washed on to the filter with 40 c.c. of 60 per cent. alcohol, and is washed successively with 40 c.c. of 60 per cent. alcohol, a mixture of 25 c.c. 96 per cent. alcohol, 10 c.c. of water, and 5 c.c. of 10 per cent. HCl, a further 40 c.c. of 60 per cent. alcohol, 25 c.c. 96 per cent. alcohol, and finally with a little ether. After being well pumped off, the tube with the starch is dried at 120° in a current of dry air for twenty minutes, cooled, and weighed. By heating the tube to redness in a current of air the starch is burnt away, and its weight, when cool, subtracted from the original weight, leaves that of the starch corresponding with 50 c.c. of the solution; multiplication by 10 gives the amount of starch in the meal originally weighed out.

When starch is to be determined in materials free from cellulose, dextrin, and other substances which give reducing substances (pentoses, &c.) with acids, the following method (Märcker and Morgen) should be used: 3 grms. of the substance, mixed with 200 c.c. of hot water, are treated with 15 c.c. of hydrochloric acid (sp. gr. 1·125) for 2½ hours in a flask immersed in a boiling water-bath and fitted with a simple reflux tube 1 metre in length. The cooled liquid is *almost* neutralised with caustic soda (it must be left faintly acid) and made up to 500 c.c., the amount of glucose in 25 c.c. being then determined by means of Fehling's solution (*see* p. 486). The quantity of starch is obtained by multiplying the amount of glucose by 0·9.

For spirit manufacture, where all materials giving fermentable substances are of importance, the new method given by Reinke is employed: 3 grms. of the amylaceous material is heated in a Lintner bottle with 30 c.c. of water and 25 c.c. of 1 per cent. lactic acid solution for two hours at 135°. The liquid is then cooled to 70–80°, shaken with 50 c.c. of hot water, cooled to the ordinary temperature, made up to 250 c.c., shaken several times during the course of half an hour, and filtered. 200 c.c. of the filtrate are heated with 15 c.c. of hydrochloric acid (sp. gr. 1·125) for two hours in a reflux apparatus immersed in a boiling water-bath. The cooled liquid is *nearly* neutralised and made up to a volume of 500 c.c., 25 c.c. being then titrated with Fehling's solution, as above.

it to the coolers and then to the wort vessels, where suitable stirrers complete the gelatinisation of the mass.

In order to avoid danger of explosion, the Henze autoclaves should be tested once a year to ascertain if they are capable of withstanding the pressure employed, since they may become weakened at rusted parts.

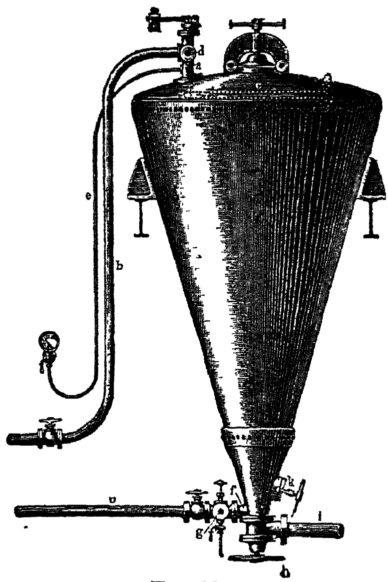


FIG. 104.

Maize, rice, and cereals are also treated in the Henze apparatus, but with the addition of 110–140 kilos of water per 100 kilos of cereals, since these contain less water (15 per cent.) than potatoes (75 per cent.), and without the water the desired fluidity of the starch would not be obtained. The volume of the autoclave is 350 litres per 100 kilos of maize. If a pressure of 5 atmos. cannot be easily attained in the autoclave, instead of using the whole grain, it is better to crush or grind it coarsely and then introduce it into the necessary quantity of boiling water in the autoclave. During the boiling, the maize should be kept in continual motion by steam-jets at the bottom and along the autoclave, or by an air-jet at the bottom with an outlet at the top, so that a spiral motion is imparted to the mass (Fig. 105). Only rarely are mechanical stirrers employed inside the autoclave. After an hour's heating the pressure reaches $2\frac{1}{2}$ atmos. and is raised to 3 atmos. in another hour. The mass is then discharged in the usual way.

Maize that is too dry is steeped in water for a day before boiling.

Maize always contains a little ready formed sugar (1·7 to 10 per cent.), and this must be allowed for in calculating the yield and also in order to avoid a too protracted heating,

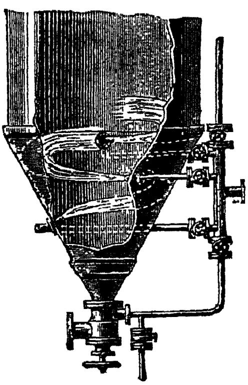


FIG. 105.

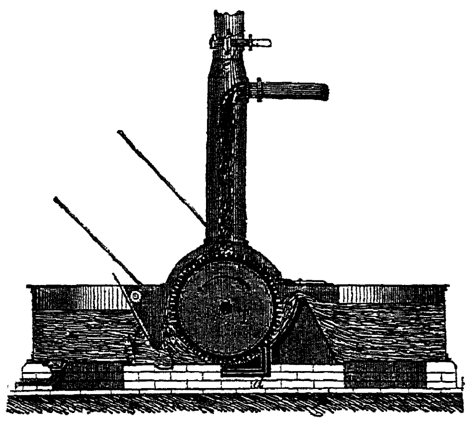


FIG. 106.

which caramelises the wort and injures it by decomposing the large proportions of fat present.

Saccharification is effected by means of malt (2·5 to 3 per cent. on the weight of maize) added to the starchy mass at a concentration of about 14° Bé. and cooled to about 50° ; if it is too cold, it coagulates and the diastase acts irregularly ; at 35–40° the lactic fermentation readily takes place ; above 65° to 70° the diastase is altered and rendered less active, dextrin being then formed in preference to maltose. The paste from the Henze autoclave is cooled in various ways, *e.g.* with Ellenberg's apparatus (Figs. 106 and 107), in which it is dropped from the top of a pipe into a vessel similar to the Hollanders used in paper factories (*see* Paper), where it is mixed, cooled, and broken up by a rotating drum, *T*, fitted with knives which graze other knives fixed to an inclined plate, *d*, at the

bottom of the vessel; the drum makes 200 revolutions per minute; above the pipe by which the paste enters is a Körting injector, *e*, which produces a strong current of air and thus facilitates the cooling of the paste during its fall.

At the present time preference is given to apparatus with centrifugal stirrers, the cooling and also the saccharification being carried out in these. Fig. 108 shows the Hentschel apparatus. The hot starch-paste from the Henze converter passes through the pipe *b* into the vessel *A*, where it is cooled by water flowing from *m* to *n* through an internal coil; the mass is mixed by means of a kind of screw, *B*, rotated by bevel-wheels outside the vessel and the air-draught is produced by the Körting injector, *r*. Fig. 109 shows a section of the Pauksch masher, in which the cooling is effected by means of water circulating through the jacket, *C*, surrounding the vessel, the liquid being mixed by four blades, *p*, which are rapidly rotated (300 revolutions per minute) by the pulley, *S*, and, as they graze the bottom of the vessel, have also a grinding action. A battery of Henze autoclaves is sometimes used in conjunction with one masher.

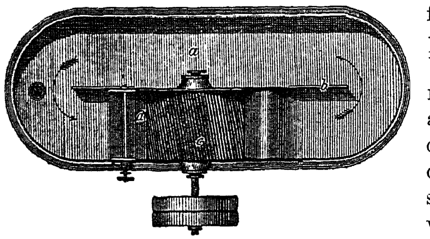


FIG. 107.

Since, during this saccharification, which may last three or four hours (and is complete when a test of the liquid, now very fluid, no longer gives the blue starch reaction with iodine solution), the mass may become infected with extraneous bacteria, which may have a harmful influence during the alcoholic fermentation of the wort, it is usually heated

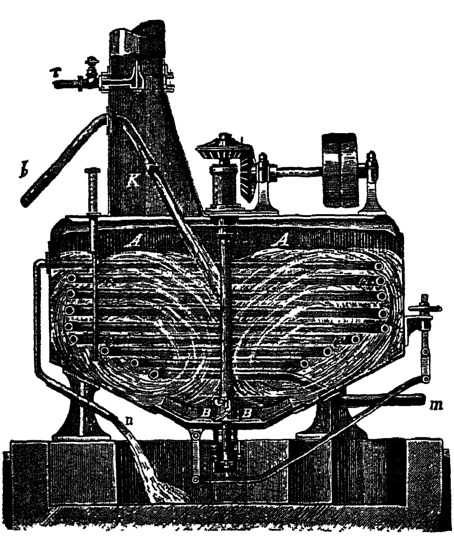


FIG. 108.

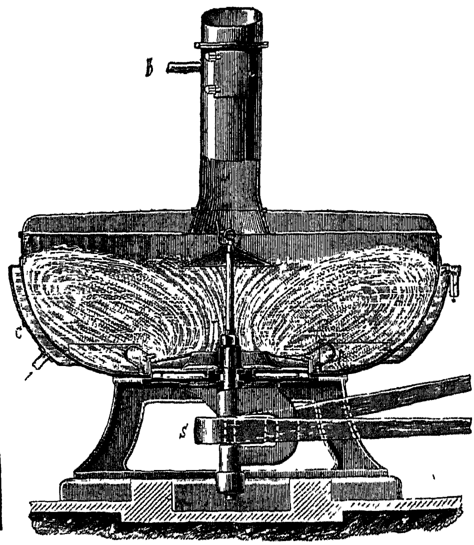


FIG. 109.

for a few minutes at 70–75° to kill these germs. This procedure has, however, the disadvantage of destroying the diastase, which can always play a part during the fermentation, and of increasing the quantity of dextrin.

In the Effront process (*see later*), the fermentation is carried out in presence of hydrofluoric acid, which kills all the bacteria but not the enzymes (previously acclimatised to the hydrofluoric acid), so that the saccharification can be effected at the most favourable temperature (55°) without subsequently heating to 75°.

As soon as the saccharification is terminated, the wort should be cooled to about 20°, and the fermentation started. This cooling may be accomplished in the masher, with suitable internal coolers (Fig. 108), but it is better done in appropriate apparatus.

One form of horizontal Hentschel *refrigerator* is shown in Fig. 111. The horizontal rotating axis (40–50 turns per minute) is formed of a tube, to which is fastened a

deep screw and in which cold water circulates from h to k. The screw moves in a horizontal cylinder through which the hot wort is forced by the screw in a direction (b to f) opposite to that taken by the water; the temperature of the wort at the outlet, f, is controlled by regulating the flow of wort and water, and, if necessary, by spraying the exterior of the cylinder with water by means of the tube l. With 700 c.c. of water, a litre of wort is cooled from 60° to 16°.

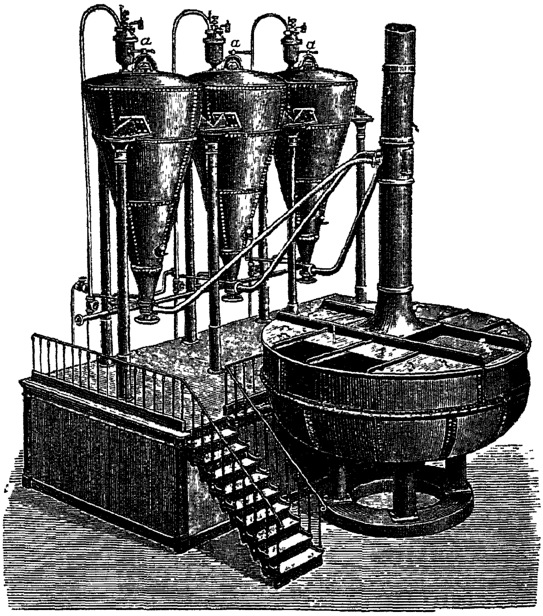


FIG. 110.

To separate the solid residue, husks, &c. (*grains*), from the wort, the latter is filtered cold through dehuskers, which have different forms, some fixed and some revolving. The most recent Pauksch type consists of a kind of centrifuge (hydro-extractor) with a fine copper gauze basket, almost like the centrifuges used in sugar factories (*see* Sugar).

Brewers and distillers often use also the Hentschel dehusker (Fig. 112 and 113), consisting simply of a rotating drum, with a spiral of metal gauze, which carries the drained grains to the middle and discharges it in cakes through doors which close automatically; the liquid flows to the bottom and passes to the fermenting vessels.

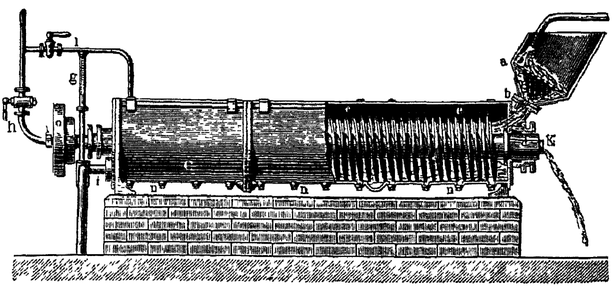


FIG. 111.

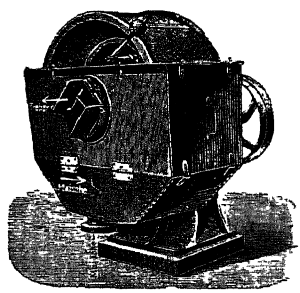


FIG. 112.

ALCOHOLIC FERMENTATION. Industrially the transformation of saccharine worts into alcoholic liquors is always effected by means of organised ferments (or yeasts). Worts left exposed to the air at 15–30° ferment spontaneously, but, owing to the different species of bacteria present, not only alcoholic fermentation, but also harmful secondary fermentations, such as the acetic, lactic, butyric, &c. (the corresponding bacteria are shown in Fig. 114), develop.

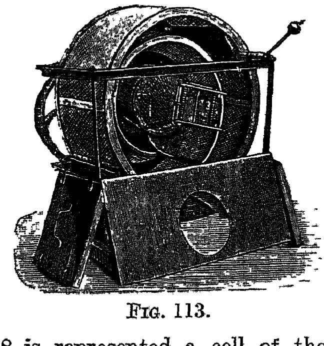


FIG. 113.

Owing to the studies of Rees and more especially of Hansen, it is nowadays admitted by everybody that the principal agent of alcoholic fermentation is *Saccharomyces cerevisiæ* (Fig. 115, *a*, *b*, and *c*), a fungus that multiplies by budding and has varying dimensions (2·5–10 μ) and appearance according as it develops at the surface (Fig. 116) or in the body of the wort (Fig. 117). In Fig. 118 is represented a cell of the ferment magnified 4000 times and showing the granulations, vacuoles, protoplasm,

cell-wall, &c. In spirit distilleries, a mixture of two varieties of yeast (top- and bottom-yeasts) is used, these being of the same race but not interconvertible; often top-yeast is preferred, as it is more active, whilst in lager-beer breweries, where the fermentation is slow, bottom-yeast is mostly used.

The final result of the decomposition of maltose by yeast can be expressed thus:

$$C_{12}H_{22}O_{11} + H_2O = 4C_2H_5 \cdot OH + 4CO_2;$$

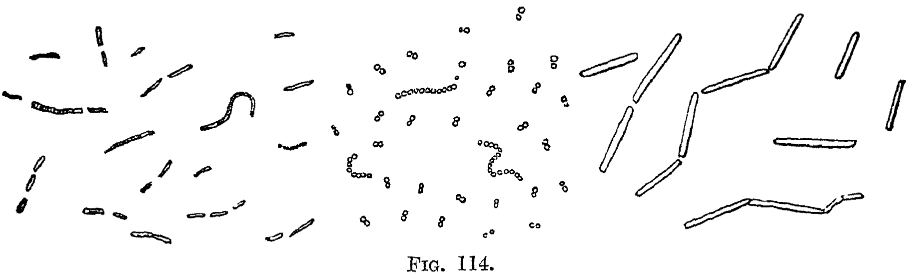


FIG. 114.

(a) Acetic bacteria (b) Lactic bacteria (c) Butyric bacteria

actually, however, the maltose and dextrin formed from the starch are transformed into glucose by the action of the maltase contained in the ferment along with the zymase, the latter then converting 95 per cent. of the glucose into alcohol and carbon dioxide

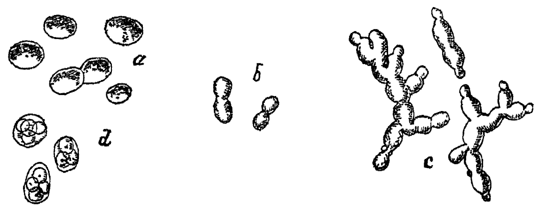


FIG. 115.

with the development of heat (if the glucose were transformed completely into $H_2O + CO_2$, the evolution of heat would be seven times as great):

$$C_6H_{12}O_6 \text{ (glucose)} = 2C_2H_5 \cdot OH + 2CO_2 + 33,000 \text{ cals.}$$

FIG. 116.

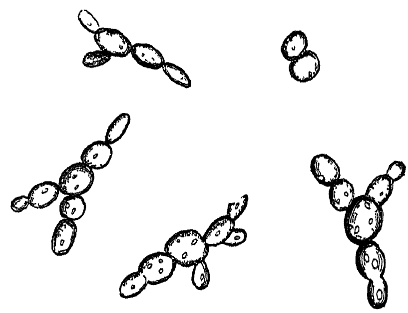


FIG. 117.

A small part of the sugar serves for the growth and multiplication of the yeast (Pasteur), about 3 per cent. of it is converted into glycerol,[1] about 0·5 per cent. into succinic acid, and the remainder into higher alcohols forming *fusel oil*, this consisting mostly of amyl alcohol ($C_5H_{11} \cdot OH$, *isobutylcarbinol*), with small proportions of isopropyl alcohol, butyl alcohols, and esters. Ehrlich

[1] The formation of *glycerol* during fermentation has not yet been explained; it is thought that it forms a direct secondary product from the decomposition of the sugar into alcohol and CO_2, or that it results from the action of lipase on the fats and oils of the ferment cells; Buchner (1906) holds that it is formed from the sugar but by a special process; Reisch (1907), however, finds no relation between the amounts of alcohol and glycerol formed and hence regards it not as a product of fermentation, but rather as a metabolic product of the yeast.

(1909) has shown, however, that fusel oil and succinic acid are formed by the decomposition of the amino-acids which constitute the cells of the ferment.

The theoretical yields of pure alcohol from various sugars are as follow:

100 grms. of	saccharose	$C_{12}H_{22}O_{11}$	—51·11 grms. or	64·6 c.c. of alcohol
,, ,,	maltose	$C_{12}H_{22}O_{11}$	— 51·11 ,,	64·6 ,, ,,
,, ,,	starch	$(C_6H_{10}O_5)_x$	— 56·80 ,,	71·8 ,, ,,
,, ,,	glucose	$C_6H_{12}O_6$	— 48·67 ,,	61·6 ,, ,,

Various sugars, however, do not ferment directly (saccharose, lactose, &c.), but must first be inverted, that is, transformed into *hexoses* (fermentable sugars with six carbon atoms), but ordinary alcoholic ferments (saccharomycetes) contain the inverting enzymes (besides zymase) and hence can effect inversion and then fermentation.[1]

The fermentation industries in general, and the alcohol industry in particular, have made marked progress since the introduction of pure ferments. The cultivation of pure

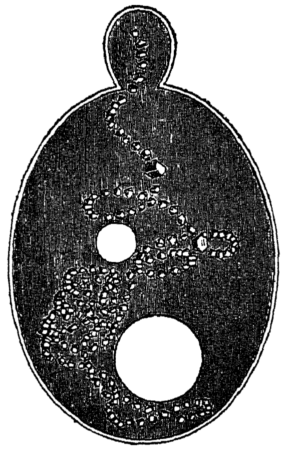


FIG. 118.

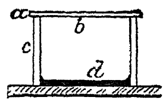


FIG. 119.

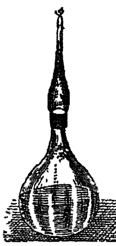


FIG. 120.

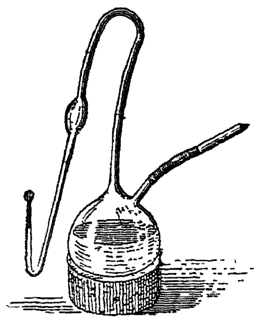


FIG. 121.

ferments has at the present time become a special industry of great importance; all precautions are taken to select and cultivate well-defined races of ferments, and this is especially owing to Hansen of Copenhagen, who, by thirty years of study and experiment, showed the great practical value of the selection of yeasts. The first pure culture is made in a *moist chamber* of glass, *c* (Fig. 119), fixed on a microscope slide, *a*; the whole is sterilised, either by a flame or by heating for two hours in an oven at 150°. Sterilised water is placed on the bottom of the chamber to keep the atmosphere moist, and the chamber placed in an incubator at 30° to 35°. The bacterial culture is developed in a drop of gelatine, *b*, adhering to the lower side of the cover-glass covering the chamber.

The culture of pure ferments can also be carried out in Chamberland flasks of 30 c.c. capacity (Fig. 120), half filled with nutrient gelatine and fermentable substances, and covered with a glass cap full of sterilised cotton-wool.

The more or less pure ferment which it is desired to cultivate is introduced by means of a sterile platinum wire into a flask containing sterile water, which is well mixed and should become just turbid. A drop of this water is then examined under the microscope in order to ascertain the number of cells of the ferment it contains. By means of a platinum wire sterilised in a flame, a drop of the water is introduced into a Chamberland

[1] According to Boysen-Jensen (1909) the *zymase* of alcoholic ferments is constituted of two enzymes: *dextrase* and *dihydroxyacetonase*, glucose first forming 2 mols. of *dihydroxyacetone* $OH \cdot CH_2 \cdot CO \cdot CH_2 \cdot OH$ (*triose*), which to a small extent can be fixed in the form of oxime or hydrazone (*which see*) by means of hydroxylamine hydrochloride or methylphenylhydrazine acetate; the dihydroxyacetonase then decomposing the dihydroxyacetone into $2CO_2$ and $2C_2H_5OH$. The dextrase alone would give directly alcohol and CO_2 if glycerol were added to the solution of glucose. With zymase (which contains dihydroxyacetonase), pure dihydroxyacetone gives alcohol and CO_2, whilst with oxydase it gives only CO_2.

flask containing liquefied gelatine at 35°. After the latter has been well shaken, a drop of the gelatine is examined microscopically on a glass micrometer (marked with crossed lines) to see that there are not too many or too few cells present, since the colonies that ultimately develop from the single cells should develop sufficiently far apart from one another not to mingle. Of this inoculated gelatine, one or more drops are placed on the cover-glass of the moist chamber, this being kept under a bell-jar until the gelatine has solidified and then placed, upside down, in the chamber. In a thermostat at 25°, the ferments are usually sufficiently developed after two or three days and the various colonies are then examined under the microscope to ascertain if one or more of them are pure, that is, constituted of similar cells of one and the same ferment. Each of the pure colonies is touched separately with a small piece of sterilised platinum wire, which is immediately dropped into a Pasteur flask (125 c.c.) charged to the extent of two-thirds with gelatine and nutritive substances (Fig. 121), the rubber tube being momentarily removed. The flask is at once closed again, and is then kept in a thermostat at 25° to 28°. After 2 days the liquid will be in a state of active fermentation, a large quantity of the ferment having been formed. Each of these flasks represents a pure culture (provided that the proper precautions have been taken in the inoculation). All the cultures are, however, examined, one or two drops from each flask being observed under the microscope.

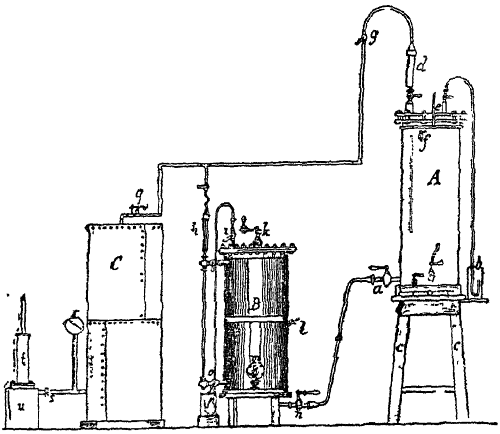


Fig. 122.

These pure yeasts or other pure ferments are largely used by brewers or distillers, who have ferments suited to their needs selected and preserved by scientific institutions, from which cultures in Pasteur flasks are despatched to them when the organisms in their own fermenting vessels begin to degenerate or become contaminated. In Fig. 122 is shown diagrammatically an apparatus for the industrial preparation of selected ferments; the metal reservoir, *C*, provided with a safety-valve, *q*, and a manometer, *r*, is filled, by means of the pump, *u*, with air filtered through a cotton-wool filter, *t*, and compressed under a pressure of 3 to 4 atmos. The vessel, *A*, is first sterilised with steam under pressure, which enters at the tap, *f*, whilst the air is driven out through the tube, *b*, dipping into a vessel of mercury forming a seal. When the cock, *f*, is shut, *g* is opened so as to allow air to filter through *d* into *A*. Hot wort is introduced into the reservoir, *A*, heated to boiling and then cooled by means of a water-spray issuing from an annular tube, *e*, and bathing the outside of *A*. The fermenting vessel, *B*, which is sterilised in the same way as *A*, is also furnished with a cotton-wool filter, *h*, and a hydraulically sealed tube, *i p*, through which the CO_2 is to escape; the glass tube, *O*, which is a continuation of the filter, indicates the level of the liquid inside the vessel. It is further provided with a vertical stirrer which is set in motion by the handle, *k*, and serves to mix the wort and yeast which are introduced through the small tap, *l*. A slight air-pressure is maintained in both *A* and *B* in order to prevent external contaminated air from entering either when the discharge-cock, *m*, for the fermented wort is opened or through any leaks there may be in the apparatus. In this way *B* can be used for a year or more without contamination taking place, a little residual yeast being left after each operation to ferment the succeeding charge of wort. The sterile wort, cooled to 15°, is passed from *A* into *B* by means of the tube, *a n*, and before it reaches the level of the tap, *l*, the pure yeast contained in a Pasteur flask is introduced through this tap; *B* is filled to the extent of about three-fourths (about 200 litres) with the wort from *A*, the whole being then well mixed. When the fermentation is ended (in three or four days with worts for alcohol production, or in 8 to 10 days for beer worts), the yeast is allowed to deposit; the fermented wort is discharged from *m* by increasing the pressure of the air and, when it

begins to issue turbid (owing to suspended yeast), m is closed and about 30 litres of wort introduced from A and well mixed in, 30 litres of the turbid yeasty liquid being then run off from B, this amount being sufficient to induce fermentation in 40 hectols. of wort in the ordinary fermenting vessels; a further quantity of 30 litres of wort is then run in from A and, after mixing, another 30 litres of yeasty wort drawn off. That remaining in B serves for the next operation. This is the procedure adopted in large breweries and distilleries; whilst in yeast-factories the wort is prepared from barley and rye under the action of malt for an hour at 60° and for about 24 hours at 40° to 44° in order to produce about 1 per cent. of lactic acid, which peptonises the proteins and so affords better nutriment for the yeast, the action being completed by the addition of 10 grms. of sodium or ammonium phosphate per hectolitre of wort. The wort is then fermented as above at 18° to 20°, and the yeast, which is formed in large quantity, is washed with water by decantation, freed from excess of water in centrifuges or filter-presses and made into a paste with 5 to 10 per cent. of potato-starch, forming cakes which are sold under the name of *pressed yeast* at about £3 12*s*. per quintal (220 lb.). 100 kilos of rye yield 16 kilos of yeast. In Germany more than 210,000 quintals of pressed yeast are produced annually, and 10,000 to 13,000 quintals exported; in five factories alone more than 110,000 quintals were made in 1909. In Italy, 1361 quintals were imported in 1905; 2000 in 1906; 3500 in 1907; 4500 in 1908; in 1909, 5300 quintals, of the total value of £21,700 (including 2000 quintals of diamalt or liquid malt worth £10,700); and in 1910, 4750 quintals, including 1137 of diamalt. Certain of the French factories export as much as 30 or 40 quintals of pressed yeast per day. In Austria, the law of May 18, 1910, regulates the trade in yeast so as to prevent adulteration and mixture.[1] In France and latterly in Italy, industrial spirit distillers are making use of the Jacquemin apparatus (Fig. 123) for the preparation of pure yeast cultures. The peptonised wort is prepared as described above, and the sterilised air, compressed by the pump A, passes through a filter of cotton-wool moistened with mercuric chloride, F, into a battery of vessels, G, the first and third of which are empty, whilst S contains sulphuric acid and n soda solution;

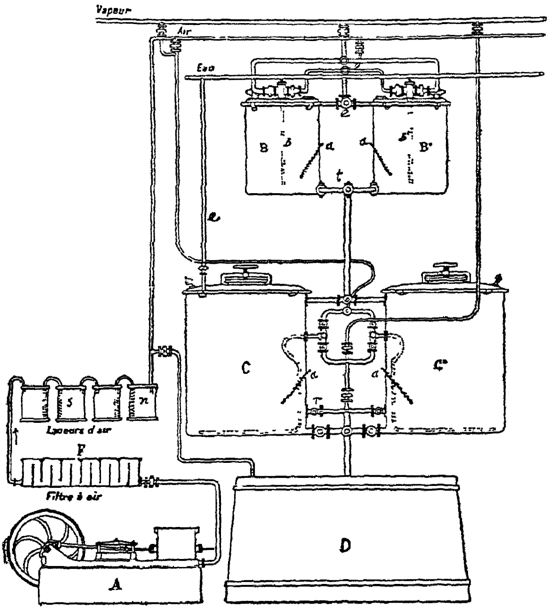


FIG. 123.

Vapeur, steam; *eau*, water; *laveurs d'air*, air-washers; *filtre à air*, air-filter

[1] Yeast Manufacture. Not only in Austria, but also in Germany, the yeast industry has lately assumed great importance, especially in spirit factories. It has given rise to special legislation and has led to the formation of powerful syndicates to regulate prices and production. The largest consumers are the bakers.

At one time, with a yield of 30 to 32 per cent. of alcohol on the weight of cereal used, the amount of yeast obtained was 12 to 14 per cent. During recent years a marked increase has been effected in the quantity of yeast (up to 20 per cent.), the yield of alcohol being diminished by vigorous aeration of the wort during fermentation (30 to 40 cu. metres of air per hour for every 100 kilos of cereals converted into wort). By the new *Braasch process* the yield of yeast can be raised to 40 per cent. and that of alcohol lowered to 15 per cent. (under some conditions of the market the production of yeast is more remunerative than that of alcohol). The value of yeast in Germany is calculated at about £3 16*s*. to £4 per quintal, and some factories produce as much as 5000 to 10,000 quintals per annum; the alcohol is valued at £1 8*s*. per hectolitre.

In the old Vienna process, worts of 10° to 20° Balling (or even heavier) were fermented by means of yeasts prepared with worts rich in lactic acid (100 c.c. of this wort should require 12 to 14 c.c. of normal sodium hydroxide solution for neutralisation). When the fermentation was complete, the yeast was collected by means of ladles and despatched along channels into vats, where its activity was arrested with cold water. After this, it was shaken on silk sieves, which retained all the husks or grains; the yeast passing through the sieves was washed two or three times with water and, after settling, pressed into cakes. In 1887–1890 all yeast factories worked on this plan, but nowadays only few of them do so.

The new aeration process starts from clear wort and green malt (non-kilned). The cereals for preparing the

the empty vessels serve as safeguards, in case the liquids are sucked backwards. The air sterilised in this way passes along suitable pipes to all the fermenting vessels, *B*, *B′*, *C*, *C′*, *D*. *B* is two-thirds filled with the peptonised wort (20 to 30 litres), which is boiled for a few minutes by steam entering through *b* and then cooled by passing a vigorous current of air through the wort and by an annular spray of water applied to the outside of the vessel *B* by the tube *e*. When the temperature has fallen to 20°, the contents of a Pasteur flask of pure yeast are introduced through the tube *a*, and the fermentation allowed to proceed for 24 hours; in the meantime, wort sterilised and cooled to 20° is prepared in *B′*; a little of the yeast is then passed from *B* through the tube *t* to *B′*, the remainder being discharged, by the three-way cock, *t*, into the larger vessel, *C*, which contains sterilised wort (250 to 300 litres). When the fermentation has reached an advanced stage (a definite *attenuation*; *see later*), the wort is discharged through the tube *r* into *D*, which also contains sterilised wort, and that remaining on the bottom of *C* is forced by compressed air into the vessel *C′*, previously charged with sterile wort.

It will be seen that, by this procedure, the working is continuous, and the yeast is renewed only once or twice per month. The yeast may then be separated from *D* and pressed, or the actively fermenting wort (5 to 6 hectols.) may be used to induce fermentation in the factory vats containing ordinary wort.

The selected yeasts are controlled practically, by measuring their fermentative activity and by determining the concentration with the microscope and cell-counters, note being taken of extraneous organisms.

Pressed yeast in cakes keeps for several days if well wrapped in paper and placed in tightly closed boxes in a cool room; otherwise it soon becomes covered with mould and unusable. When the stock of yeast is larger than is required, it can be dried at a cost of a shilling per quintal and sold as a good cattle food. To prevent secondary fermentations from taking place, instead of the lactic acid fermentation, during the preparation of selected yeasts, Bücheler (Ger. Pat. 123,437) suggests the addition of 180 c.c. of concentrated sulphuric acid to every hectolitre of wort; the process yields excellent results in practice, notwithstanding the disputing of the patent from 1900 to 1909, owing to the fact that a similar patent (No. 3885) was granted in Austria to Bauer in 1900.

FACTORS WHICH FACILITATE OR RETARD FERMENTATION. Alcoholic fermentation may be hindered by various factors. Very concentrated sugar solutions do not ferment, whilst with a concentration of 70 per cent., only 6 per cent. of the sugar is converted into alcohol; with a strength of 60 per cent., 25 per cent. is transformed, and when the concentration is 30 per cent. it is possible, although not without difficulty, to convert 92 per cent. of the sugar into alcohol.

Temperature has also a very marked influence on alcoholic fermentation, and at 0° or at 60° it ceases completely; later we shall see at what temperature the process takes place most regularly from the point of view of the industrial yield.

Alcohol, although a product of fermentation, when it reaches a certain concentration, may prevent further fermentation. And this anti-fermentative action of the alcohols is, to some extent, proportional to their molecular weights. Thus the fermentation of glucose can be arrested by 20 per cent. of methyl alcohol, 16 per cent. of ethyl alcohol, 10 per cent. of propyl alcohol, 2·5 per cent. of butyl alcohol, 1 per cent. of amyl alcohol, and 0·1 per cent. of capryl alcohol.

mash and then the wort are no longer ground, but are softened with water and then crushed. The mashing of the green malt is carried out in a medium slightly acidified with sulphuric acid, the lactic ferment (*Bacillus Delbrückii*) being allowed to act, after the diastase, for several hours at 40° to 50°. When the desired acidity is reached, further acidification is prevented by heating the whole mass to 68° to 70° (the total amount of sulphuric and lactic acids, without CO_2, corresponds with 5 c c. of normal NaOH per 100 c.c. of wort). The concentration of the wort used was at one time 12° to 14° Balling, but at the present time 10° Balling is preferred. The temperature of fermentation is about 25°. If the acidity of the wort is less than 2 c.c. of normal soda per 100 c.c., the yeast obtained is flocculent and separates badly. The separation of the yeast is now effected thoroughly and rapidly in centrifuges. The fermentation is started by adding to the wort 4 to 5 per cent. of yeast (calculated on the weight of cereals used) and is finished in 10 to 12 hours; the yield of 40 per cent. (on the weight of cereals) of yeast is in addition to the amount added (5 per cent.). The yeast cultures should be renewed occasionally.

The fermented wort is feebly alcoholic (less than 1 per cent. of alcohol), so that the distillation and rectification necessary to obtain 90 to 95 per cent. alcohol are very expensive; further, the alcohol is not of good quality and is hence only suitable for denaturing. The diminished yield of alcohol is due partly to loss of the alcohol carried away by the large volumes of air passed through the wort and partly to destruction of maltose by ferments or enzymes developing in presence of excess of air. The less the amount of air used, the greater is the amount of spirit obtained.

In the control of the purity of the yeast, account must be taken of the extraneous ferments, of the quantity of starchy substances (when starch is not added this does not reach 4 per cent.) and of the fermentative activity.

ANTISEPTICS, in general, prevent fermentation when they are present in relatively great concentrations ; they may, if their dilution is great, exert a favourable influence on fermentation.[1]

However, since the favourable action exhibited by these solutions depends on the quantity of yeast present and that of the antiseptic dissolved, it is possible, when the quantity of yeast is large, that solutions more concentrated than those indicated in column (B) may produce favourable effects on the fermentation. It is unnecessary to state that these concentrations vary somewhat with the nature of the organisms. It has been shown recently (1910), for example, that *Staphylococcus pyogenes aureus* resists a 2·7 per cent. solution of mercuric chloride for six hours.

The organic acids also exert an unfavourable influence on alcoholic fermentation,[2] whilst, within certain limits, lactic and formic acids and formaldehyde have a beneficial action, since they prevent the development of harmful bacteria and are readily tolerated by alcoholic ferments specially *acclimatised* to their action. By adding small quantities of formaldehyde and of sterilised milk (which then gives lactic acid), the yield of alcohol has recently been increased by as much as 2 per cent. E. Soncini (1910) has shown that the course of fermentation in general is closely connected with the chemical medium in which it takes place ; thus, in a saccharine wort (from bananas), the lactic fermentation first develops spontaneously and proceeds until the lactic acidity reaches a certain limiting amount ; this may be followed by alcoholic fermentation, which, in its turn, may be succeeded by the acetic fermentation ; the lactic fermentation may ultimately begin again. It is only by considering all these conditions that a regular alcoholic fermentation and a good yield of pure alcohol can be assured, since in general the secondary and harmful products of the fermentation (higher alcohols, such as amyl, &c.) result from the actions of extraneous micro-organisms. The carbon dioxide formed during fermentation may give rise to pressures as high as 12 atmos. if hermetically sealed vessels are used, and the action of the yeast is then retarded or even arrested.

PRACTICE OF FERMENTATION. To start the fermentation of the worts prepared as described above, various methods are used: in some cases a portion of old, fermented wort from a preceding operation is employed ; but this is not a rational method, because the yeast in the old wort is in a condition unfavourable to development and is also contaminated with other micro-organisms which would develop readily in the new wort. To be preferred is the custom followed by certain distilleries of starting the fermentation with brewery yeast, which is cheap and comparatively pure. The best and most rational method is, however, the use of selected yeast in culture wort or in a pressed condition (*see above*), as supplied by various firms and institutions which guarantee its purity. By this means alone it has been possible during the past few years to increase the mean yield of alcohol in distilleries by 0·5 per cent. or even 1 per cent., and at the same time to improve the quality of the product.

It is advisable to ferment worts as soon as they are prepared and cooled to 15° to 20°, delay resulting in contamination with heterogeneous germs always present in the air.

To avoid secondary fermentations as far as is possible, addition is often made to the

[1] Thus, for example :

	(A) *The most dilute solution capable of preventing fermentation is :*	(B) *The most concentrated solution capable of favouring fermentation is :*
Mercuric chloride	1 in 20,000	1 in 300,000
Potassium permanganate	„ 10,000	„ 100,000
Bromine	„ 4,000	„ 50,000
Thymol	„ 3,000	„ 20,000
Salicylic acid	„ 1,000	„ 6,000
Phenol	„ 200	„ 1,000
Sulphuric acid	„ 100	„ 10,000
Boric acid	„ 25	„ 8,000

[2] The action of some of the commoner acids is as follows :

	Dose that retards alcoholic fermentation	Dose that arrests alcoholic fermentation
Acetic acid	0·50 %	1·0 %
Formic „	0·20 %	0·30 %
Propionic acid	0·15 %	0·30 %
Valeric „	0·10 %	0·15 %
Butyric „	0·05 %	0·10 %
Caproic „	—	0·05 %

wort of antiseptics, to which the selected yeasts have been habituated. Thus, small proportions of calcium bisulphite or, better, of ammonium or aluminium fluoride are added, the hydrofluoric acid—liberated under the action of the acids formed in the secondary fermentations—killing the harmful organisms. With the Effront process, hydrofluoric acid (*see* vol. i, p. 156) is added directly in the proportion of 5 or even 10 grms. per hectolitre of wort (some yeasts resist as much as 100 grms. of HF per hectolitre). Sometimes a selected lactic ferment (*Bacillus acidificans longissimus*) is added, this also favouring the production of pure alcohol.

The use of these yeasts acclimatised to the action of hydrofluoric acid renders possible the employment of the temperature 55° to 57° (*see above*) for the previous saccharification of the starch by diastase, this low temperature resulting in the formation of an increased amount of maltose; also if there are other noxious living micro-organisms in the wort, these are killed by the hydrofluoric acid during the fermentation.

Effront, however, succeeded in preparing yeasts capable of fermenting also the dextrin with ease; when these are used, the saccharification with diastase can be effected with less malt and at 64° to 65°, so that harmful micro-organisms are killed. All the apparatus, instruments, and vats which come into contact with the wort should be previously washed with dilute hydrofluoric acid solution (100 grms. per 25 litres of water).

For every hectolitre of wort are added about 30 grms. of pressed yeast in small quantities mixed up with increasing quantities of wort and well stirred in; the fermentation then starts immediately.

The fermentation of the wort proceeds in three successive phases:

(1) *Preliminary fermentation*, in which the yeast develops and grows, the most favourable temperature being 17° to 21°.

(2) *Principal fermentation*, in which the maltose and glucose are fermented, best at 26° to 30°.

(3) *Secondary fermentation*, in which the dextrins are fermented, the diastase continuing to saccharify the remaining dextrins as the wort becomes warm, the best temperature being 25° to 27°.

The vats, holding 10 to 90 hectols. and often furnished with stirrers, are filled with wort to the extent of nine-tenths. The temperature is regulated by suitable cold-water coils (attemperators, Fig. 124), which are of various forms (*see* Beer). In general, these attemperators have a surface of 0·3 to 0·4 sq. metres per 10 hectols. of wort. Fermentation is begun in the vats at 12° to 15°, and after 2 or 3 hours the temperature rises and the fermentation becomes vigorous. The liquid is then agitated to liberate the CO_2, thus diminishing the pressure in the mass and facilitating the fermentation, the temperature not being allowed to exceed 28° to 29°. After two days, the principal fermentation ceases and the temperature is maintained at 25° to 26° for a day, the fermentation being thus completed.

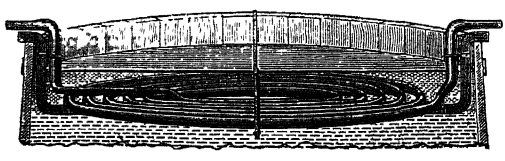


FIG. 124.

Worts that are too dilute or are made from poor malt or impure grain give a boiling fermentation that hurls the liquid from the vat and renders the subsequent distillation difficult. This inconvenience is avoided by using more concentrated worts and good yeast, or, in case of necessity, adding 100 to 200 c.c. of oil to each vat.

Ammonium fluoride (2 to 2·5 grms. per hectolitre) or hydrofluoric acid (rather less) is often added to the wort before fermentation.

LOSSES AND YIELDS. A residue of unfermented starch (0·7 to 2 per cent.) and dextrin (5 to 8 per cent.) always remains after fermentation. In every fermentation 2 to 3 per cent. of glycerol are formed; also part of the sugar serves as food for the yeast and part of the alcohol evaporates, this making a total of 6 to 8 per cent.

Starting with 100 parts of starch, 12 to 20 parts are usually lost in various ways, and with improper working the loss may reach 28 per cent.

If the starch could be transformed *theoretically* into alcohol and carbon dioxide alone, 100 kilos of starch should yield 71·6 litres of pure alcohol; allowing for these losses and

working under the best conditions, 63·5 litres of alcohol are obtained; 60 litres is a good yield and 58 litres a medium one, whilst 55 litres would indicate bad conditions of working. The mean starch-contents of many of the prime materials used in the distillery are given on p. 117; that of green malt (from good barley) is 38 to 42 per cent. and that of kilned malt, 65 to 70 per cent. Whilst in 1883 Italian distilleries gave an average yield of 31·5 litres of alcohol per quintal of maize, in the season of 1904–1905 the yield (official statistics) amounted to 35 litres.

For calculating the yield, the exact analyses of the prime materials, starch and sugar, must be known. The sugar-content of a wort is determined from the density by means of the Balling *saccharometer* modified by Brix, *degrees* Brix (or Balling) read at 20° (formerly 17·5°) indicating directly the percentage of sugar in the solution. In worts, however, part of this density is due to unfermentable substances.

As fermentation proceeds, the proportion of alcohol increases and the density diminishes; this diminution is called the *degree of fermentation* or *attenuation*. The density is measured before, during, and after the fermentation on the filtered wort, and if it filters badly it is diluted with a *definite* volume of water.[1] When the fermentation is finished and the degree of attenuation controlled, the resultant fermented wash (with about 9 to 11 per cent. of alcohol) is subjected to distillation and rectification in order to extract the alcohol and separate it from the water, yeast, and other solid and liquid substances. Before the distillation apparatus is described, certain special saccharification and fermentation processes, which have been recently applied practically, will be considered.

The **AMYLO PROCESS** (Collette or Boidin Process). This process is based on investigations of Calmette, Collette, Boidin, and others, who found that certain *Mucors* (moulds, *see* p. 111), isolated from impure Chinese and Japanese ferments, are capable of performing the functions of both diastase and zymase, that is, of transforming starch into alcohol by

[1] The density, p, before fermentation is due to x parts of sugars + z parts of non-fermentable substances; if the density after fermentation indicates the magnitude, z, then $p - z = x$. But this does not give the absolute attenuation, since z is altered by the presence of alcohol and carbon dioxide. If the carbon dioxide is eliminated by shaking and gentle heating, a density, m, is obtained and the magnitude of $(p - m)$ gives the so-called *apparent attenuation* (apparent because alcohol is still present); the amount of alcohol formed can be allowed for by means of a factor, a, the *real attenuation* being given by $A = a\,(p - m)$. The value of a is determined by distilling a small quantity of fermenting wort, and calculating the value of the expression $a = \frac{A}{(p - m)}$; a is, however, not a constant, but varies with the nature of the sugars, with the original concentration, p, and with the stage of the fermentation (incipient, vigorous, or secondary). If a is known, the quantity of alcohol obtainable from a *fermented* wort of a given density can be calculated.

The ratio between the *apparent attenuation*, $(p - m)$, and the original saccharometer reading, p, gives the so-called *degree of apparent fermentation* (B). If $p = 25°$ and the density (m) of the fermented wort is 3, we have $B = \frac{25 - 3}{25} = 0{\cdot}880$, which is the *degree of apparent fermentation* and indicates that, of every unit of saccharine substances, 0 880 parts have disappeared, *i.e.* have been fermented. From the degree of apparent fermentation (B), the degree of apparent attenuation can, of course, be obtained: thus, $\frac{p - m}{p} = B$ gives $p - m = Bp$; and from the factor a mentioned above, the amount of alcohol resulting from such degree of apparent fermentation is known

The *real attenuation* (A') is determined by distilling a certain quantity of the fermented wort until its volume is reduced to one-third, the residue being made up to the original volume with water and the density, n, measured; the real attenuation then $= p - n$. But, since the residue always contains unfermented matter, in order to calculate the alcohol, a factor, b, is determined in the same way as the factor, a, *i.e.* by distillation of a part of the fermented wort; the quantity of alcohol can then always be determined from the density of the fermented wort, for, since $A' = (p - n)\,b$, $b = \frac{A'}{p - n}$. Similarly, the *degree of real fermentation* will be $B' = \frac{(p - n)}{p}$ which expresses the fraction of the extract (dissolved substance without alcohol) really fermented, the manufacturer being thereby able to judge if the fermentation proceeds normally and to establish comparisons with previous fermentations, &c.

The apparent attenuation (alcohol being present) is always greater than the real (derived after elimination of the alcohol) and the *attenuation difference*, D, is obtained by subtracting one from the other, $(p - m) - (p - n) = D$. This magnitude, D, is therefore equal to $n - m$ and increases as the fermentation proceeds towards completion; also here the quantity of alcohol already formed is found by determining experimentally a factor, c, in the usual way, so that $\frac{A}{n - m} = c$, or $A = (n - m).c$. The ratio of the apparent to the real attenuation, $\frac{p - m}{p - n} = q$, gives a *quotient of attenuation* which varies with the concentration of the liquid but becomes constant towards the end of the fermentation and shows how much the apparent fermentation is greater than the real; by its means, almost all the saccharometric calculations can be made: $\frac{b}{q}$ = the alcohol factor for the real attenuation, and if this is divided by q diminished by unity [*i.e.* by $(q - 1)$], the factor, c, for the difference of attenuation is obtained The factor, c, is used for the analysis of liquids for which the value of p is unknown also $\frac{B}{q} = B'$ (*degree of real fermentation*).

The following illustrates a practical calculation: the original saccharometric degree of a wort was $p = 16{\cdot}2$, and that after fermentation $m = 1$, and that after boiling $n = 3{\cdot}9$; applying any one of the three factors (a,

way of maltose and dextrin. Of these moulds, *Amylomyces Rouxii*, discovered by Calmette in 1892, and the *Mucors B* and *C* discovered by Collette, Boidin, and Mousain, are of most importance industrially.[1] Of the first two, the forms observed under the microscope in different stages of development are shown in Fig. 125 (*A*, *B*, *C*, *D*, and *E*).

b, and *c*) given in the appended Table, the *apparent attenuation* becomes $A = (p-m)\,a$ (where $p = 16{\cdot}2$, $a = 0{\cdot}4267$) $= 6{\cdot}4858$ per cent. of alcohol. Calculating according to the *real attenuation*, $A = (p-n)\,b$ (where $p = 16{\cdot}2$ $n = 3{\cdot}9$, and $b = 0{\cdot}5274$) $= 6{\cdot}4870$ per cent. of alcohol. Lastly, calculating from the *attenuation difference*, *D*, $A = (n-m)\,c$ (where $c = 2{\cdot}2350$) $= 6{\cdot}4815$ per cent. Hence the fermented wash consists of 6·48 per cent. of alcohol, 3 9 per cent of unfermented extract (*n*), and 89 62 per cent of water.

TABLE FOR CALCULATING THE ATTENUATION IN FERMENTED WORTS

Saccharometer degrees of the wort	Alcohol factors for the attenuation		Factors for the attenuation difference	Attenuation quotient	Values of $\frac{c}{b}$
	Apparent	Real			
p	*a*	*b*	*c*	*q*	
6	0·4073	0·4993	2·2096	1·226	4·4247
7	0·4091	0·5020	2·2116	1·227	4·4052
8	0·4110	0 5047	2·2137	1·228	4·3859
9	0·4129	0·5074	2·2160	1 229	4·3668
10	0·4148	0 5102	2·2184	1·230	4·3478
11	0·4167	0 5130	2·2209	1·231	4·3289
12	0·4187	0 5158	2 2234	1 232	4·3103
13	0·4206	0 5187	2·2262	1 233	4·2918
14	0 4226	0 5215	2·2290	1 234	4 2734
15	0·4246	0·5245	2·2319	1·235	4 2553
16	0·4267	0 5274	2·2350	1·236	4·2372
17	0 4288	0·5304	2·2381	1·237	4 2194
18	0 4309	0 5334	2·2414	1·238	4·2016
19	0·4330	0·5365	2·2448	1 239	4·1840
20	0·4351	0 5396	2·2483	1·240	4 1660
21	0·4373	0·5427	2 2519	1·241	4·1493
22	0·4395	0 5458	2·2557	1·242	4·1322
23	0·4417	0·5490	2 2595	1·243	4·1152
24	0·4439	0 5523	2 2636	1·244	4·0983
25	0·4462	0·5555	2 2677	1·245	4·0816
26	0·4485	0·5589	2·2719	1·246	4·0650
27	0·4508	0·5622	2·2763	1·247	4·0485
28	0·4532	0·5636	2·2808	1·248	4·0322
29	0·4556	0 5690	2·2854	1·249	4·0160
30	0·4580	0 5725	2·2902	1·250	4·0000

B. Wagner, F. Schultze, and J. Rüb (1908) suggest the Zeiss immersion refractometer as a means of determining the *attenuation*: exact results are obtained rapidly and with a small quantity of liquid (20 to 30 c.c.). A little of the wort is well shaken to get rid of carbon dioxide, and filtered through a covered filter, 5 c.c. of the filtrate being used to determine the refractometer reading, *A*, at a temperature of 17·5°; a further 20 c.c. are evaporated to one-half the volume in a porcelain dish to expel the alcohol, the volume being then made up exactly to 20 c.c. with water and the refractometer reading, *B*, taken. From the difference, $A-B=C$, 15 (the refractometer reading for water) is subtracted, giving *E*; the corresponding alcohol degree (by volume), *V*, is then found in the following Table and can be subsequently corrected for the density of the wort:

E:	16·2	17·5	18·8	20·1	21·4	22·8	24·2	25·6	27·1	28·6	30·1	31·7	33·3	34·9	36·4	38·0
V:	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16

[1] Among the *Hyphomycetes* (moulds, p. 111)—in the *Mucor* and *Mucedinæ*—Pasteur found certain varieties (*Mucor racemosus*) capable of transforming sugar into alcohol and carbon dioxide when they live immersed in the liquid out of contact of air (like the yeasts); in presence of air, they convert the sugar directly into water and carbon dioxide. These are called *facultative anaerobic* organisms. In 1887 Gayon studied other varieties which behave similarly (*Mucor alternans*, *spinosus*, and *circinelloides*), and Prinsen Geerligs investigated *Chlamydomucor oryzæ*, which is used in Java to ferment molasses In 1892 Calmette imported from China, studied, and named *Amylomyces Rouxii*, the *Mucor* isolated from the rice-ferment used by the Chinese (which is more active than the Japanese *koji*) for the preparation of spirit; later he found this *Mucor* in rice-husks. At Tokyo in 1894, Takamine studied, and applied practically to the saccharification of rice, *Aspergillus oryzæ* (separated from Japanese *koji*, which is a mixture of yeasts and moulds used in Japan for producing alcoholic fermentation), but it did not meet with success, owing to its action being too energetic. Boidin, Collette, and Mousain investigated *Mucor β*, which is another *Mucor* separated from Japanese koji and is different from, and more important industrially than, that of Takamine; *Mucor γ*, which was separated at the same time from Tonkin rice, is of still greater practical value than *Mucor β*.

These moulds have the special property of saccharifying starch and of fermenting the sugar thus formed. Their saccharifying and fermentative activity is, however, influenced by the acids that they produce. Thus, *Amylomyces Rouxii*, which was the first to be used in practice in 1898, was abandoned later, as it transforms rather too much sugar into carbon dioxide and water and, owing to the production of 1 45 grms. of acid per litre of wort (at

Collette and Boidin patented in 1897 (Eng. Pat. 19,858) a process for the industrial utilisation of *Amylomyces Rouxii* for manufacturing alcohol directly from the starch of cereals, &c., and later they utilised *Mucor* β. At the present time this process is employed on an enormous scale in various distilleries in France, Belgium, and Italy (at Savona).

As it is necessary to work with perfectly aseptic worts, the starch-paste prepared in the ordinary way with the Henze apparatus is passed into closed metal cylinders holding 200 to 1000 hectols. and furnished with vertical stirrers. When the temperature reaches 65°, 1 per cent. of malt (on the amount of maize used) is added to render the mass rather more liquid; after an hour the mash is slightly acidified by the addition of 0·1 grm. of sulphuric acid per litre, and is then rendered completely sterile by passing steam in at the bottom and boiling the wort until the steam issues freely from the upper aperture. The apparatus is then closed hermetically, a vacuum being produced by the condensation

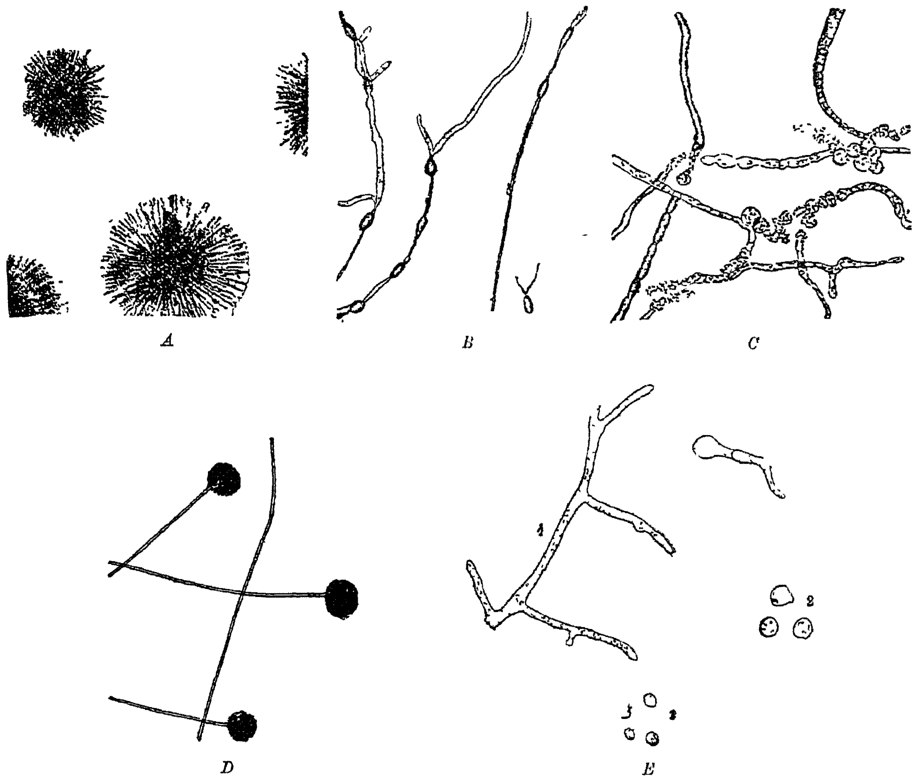


FIG. 125.

A. Colonies of *Amylomyces Rouxii* in wort-gelatine. *B*. Mycelial conidia of *Amylomyces Rouxii* in aerobic cultures. *C*. Segmentation into gemmæ of the mycelium of *Amylomyces* in anaerobic culture. *D*. Hyphæ of *Mucor* β (1 : 100) with sporangia in aerobic culture. *E* Mycelium of *Mucor* β with spores in different stages of development in anaerobic culture: 1, spores just separated; 2, turgid spores ready to germinate; 3, germinating spores; 4, mycelium (1 : 600).

of the steam. The vacuum is relieved by allowing sterilised air—filtered through cotton-wool (*see* p. 124)—to enter; the maintenance of a slight pressure inside the vessel prevents the entry of germs. By stirring the starch and running cold water down the outer walls of the cylinder 1000 hectols. of boiling wort may be cooled in five hours to 38°; this is the most suitable temperature for the *Mucor* fermentation, but a great part of the

16° Balling), complete attenuation is obtained only in very dilute worts (7° to 8° Balling, these giving 4 to 4·5 per cent. alcohol); *Mucor* β, on the other hand, forms only 0·75 grm. of acid, and can ferment worts at 10° to 17° Balling (which give 8 to 9 per cent. of alcohol) without oxidising completely more than a very small proportion of sugar.

Calmette studied more particularly the saccharifying properties of *Amylomyces Rouxii*, but in 1897 Boidin and Rolants, and simultaneously Sanguinetti (Institut Pasteur, 1897) found that this mould is also capable of transforming sugar and dextrin into alcohol; it was found later that *Mucor racemosus*, which had been already studied by Pasteur, behaved similarly. In 1895 Professor Saito, of Tokyo, isolated *Rhizopus oligosporus*, which acts like *Amylomyces Rouxii*.

sulphuric acid added must first be neutralised. A vat of 1000 litres capacity contains 150 to 200 quintals (15 to 20 tons) of maize and six times as much water.

The *Amylomyces* is cultivated in the laboratory on 100 grms. of rice and 200 c.c. of sterile wort, so that preferably spores are developed. Every culture-flask contains a total of about 0·1 grm. of spores, and this quantity is sufficient to inoculate 1000 hectols. of wort. The *Mucor* is introduced, under aseptic conditions, into the vats from above and the stirrer set in motion; a little air is introduced, this issuing by an upper tube with a hydraulic seal. In the course of 24 hours the wort is attacked by an abundant growth of the *Mucor*. The mass is then cooled to 33° and, in order to complete the alcoholic fermentation more rapidly, a small quantity of ordinary yeast (500 c.c. of a wort culture, corresponding with 3 to 4 grms. of pressed yeast) is added.

After 3 to 4 days, the alcoholic fermentation is complete (the carbon dioxide passes out at the top through the water-seal). Fig. 126 shows diagrammatically a plant with five large fermentation vessels.

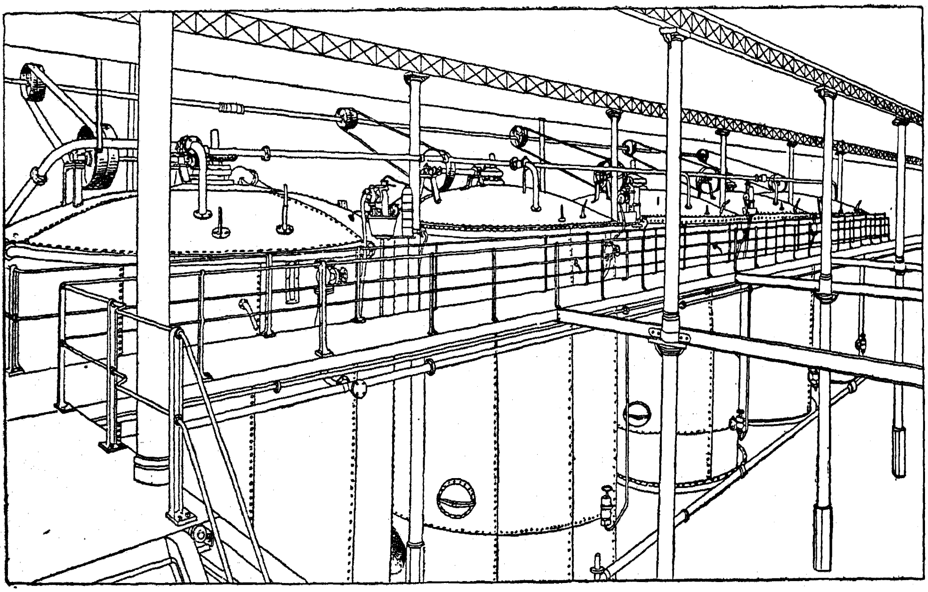


FIG. 126.

The advantages of the amylo-process are: (1) a considerable saving in malt, only about 1 per cent. being used instead of 12 to 15 per cent. by the old process; further, air-dried malt is difficult to keep in hot countries; (2) the reduction of the amount of yeast required to a minimum. The yield of alcohol is also sensibly increased, one quintal of maize containing 57 to 58 per cent. of starch yielding 37·5 litres of alcohol, *i.e.* 65 (often 66) litres of pure alcohol per 100 kilos of starch; the old method of working gives only 60 to 61 litres.

The increase in the alcohol-yield is naturally due to the fermentation taking place in a wort uncontaminated with extraneous micro-organisms; on rectification, 4 to 5 per cent. more good spirit (*bon goût*) are obtained than by the old process.

Finally, the spent wash (residue after distillation) filters better, since it contains less dextrin and does not block the filter-presses.

DISTILLATION OF THE FERMENTED LIQUID. As has already been stated, the fermentation is rendered the more complete by using worts which are not too concentrated and yield 9 to 10 per cent. of ethyl alcohol. These fermented liquids contain also

small quantities of various other substances, such as aldehydes, organic acids (acetic, propionic, butyric, lactic, succinic, &c.), certain higher alcohols (amyl, propyl, butyl; glycerol), &c., besides the solid residues of cereals and yeast and small amounts of unfermented dextrin and starch.

It was formerly not easy to separate the ethyl alcohol from these products, in spite of the great differences in boiling-point in some cases (amyl alcohol, 132°; ethyl alcohol, 78·4°), and, as already explained on p. 109, this separation cannot be effected with the most exact fractional distillation, so that recourse must be had to *rectification* (*see* p. 3).[1]

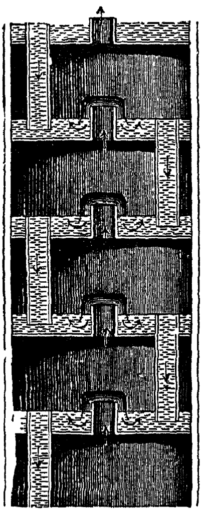


Fig. 127.

Every distillation apparatus is now composed of four parts: (1) the boiler in which the alcoholic liquid is heated; (2) the rectifier; (3) the dephlegmator; and (4) the condenser. The liquid collecting in the dephlegmator returns to the column (hotter), where alcohol vapours are formed richer than those from which it was formed in the first distillation; so that the alcohol vapours of the dephlegmator, uniting with the other vapours before the condenser is reached, contribute to form a more concentrated alcohol.

Apparatus with continuously working columns and with recovery of the heat have been studied and applied since 1867 (Savalle).

The action of a rectifying column may be understood from Fig. 127, showing part of the column, which is divided into a number of chambers communicating by means of tubes and placed above the boiler. The mixture of alcohol and water vapours from the boiling fermented wash below ascends the column from chamber to chamber through the central tubes, which are covered with caps dipping below the surface of the liquid in the chambers; by this arrangement the mixed vapours are obliged to pass through the hot, condensed liquid, which slowly descends the column through the drop-tubes, when it reaches a certain level in each chamber. The vapours give up to the liquid mainly water-vapour, and the liquid gives up to the vapours preferably the alcohol it contains, so that the alcohol-vapour reaches the top of the column mixed with only a little water-vapour and passes to the condenser, whilst water almost free from alcohol flows downwards, forming *vinasse* or spent wash.

With this column, 8 to 10 metres high and containing 20 to 25 plates and chambers, one distillation and partial rectification yields directly a crude 50 to 65 per cent. alcohol, and when this is subjected to a second similar distillation and rectification a concentration of 90 per cent. or even 96 per cent. is attained; each apparatus gives a high output. This is the procedure often adopted in France.

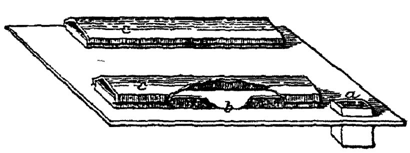


Fig. 128.

Taller columns (14 to 18 metres) are, however, used, especially in Germany, and these with efficient dephlegmators give 90 per cent. or even 96 per cent. alcohol in one continuous, although slower, operation. The *cylindrical* columns are advantageously replaced by *square* ones, which are less easily stopped up and more easily cleaned and repaired; in place of the costly copper columns, cheaper cast-iron ones are now largely used. A square plate of such a Savalle column is shown diagrammatically in Fig. 128, the apertures and

[1] The first forms of distillation apparatus were used in the times of the ancient Arabs, and were termed *alembics*. The alchemists made improvements in the shape, especially of the part used for condensing. Simple distillation apparatus, like that used for obtaining distilled water (vol i, p. 225), yield a highly aqueous spirit, termed *phlegm*. Argand, and later Adam (about 1800), utilised the heat of the aqueous alcoholic vapours distilling over to heat the liquid to be distilled. Solimani and Berard (1805) improved the apparatus so as to allow a distillate moderately rich in alcohol to be obtained in a single operation. Before the condenser was placed a vessel called a *dephlegmator*, which condensed part of the water-vapour and part of the alcohol (*phlegm*), more concentrated alcohol vapours passing to the condenser. The first really rational and complete apparatus for the fractional distillation of alcohol was constructed by Cellier-Blumenthal (1815), who used dephlegmators and the first rudimentary rectifiers; but as early as 1813, A. Baglioni had placed semi-rectifying dephlegmators directly above the boiler.

The first column rectifying dephlegmator was devised by Derosne and Cail in 1817, and shortly afterwards widespread use was made of the very convenient Pistorius apparatus, with its flat, lenticular dephlegmators, which allows of 60 to 75 per cent. alcohol being obtained directly, and is still used in some of the smaller distilleries.

tubes being sufficiently wide to avoid obstructions when dense fermented worts, rich in solid matters, are distilled. The heating of the column and of the liquid is no longer effected by direct steam, as this causes useless dilution ; indirect steam is employed with

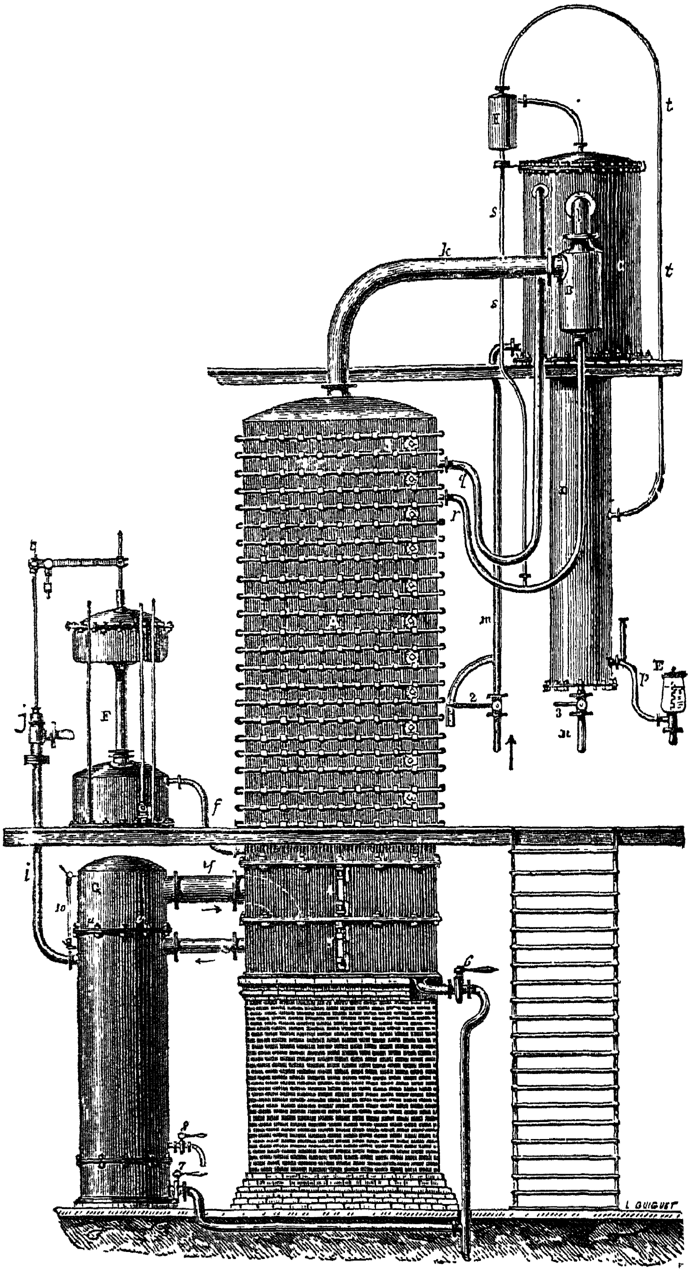


FIG. 129.

a tubular heater, to be described later. In order to obtain regularity of working and constancy in the alcoholic strength an automatic steam regulator is used (*see below*), and the supply of fermented wash to the apparatus is so controlled that the yield and strength of the alcohol remain uniform. The heat of condensation of the alcohol vapours is recovered to heat the wash, and the latter, before being introduced into the top of the

column, is passed through tubular heaters so as to utilise also the heat of the spent wash before this is discarded.

Fig. 129 shows the whole of a Savalle continuous distilling apparatus. The wash to be distilled passes from large constant-level tanks, situate on the upper floors, through the tube *m*, furnished with a regulating cock, 2, into the bottom of the heater, *C*, from which it issues at the top, after serving to condense the alcohol vapours coming from the column by the tube *k*; these vapours, however, first yield a little condensed spirit in *B*, this being carried to the column by the tube *r*. The heated wash passes along the pipe *q* to the top of the column and slowly descends, meeting meanwhile the ascending vapour current, to which it gradually gives up its alcohol, as stated above (*see* Fig. 127). The alcohol condensed in the wash-heater is cooled in the condenser, *D*, below, through which cold water circulates. If the wash is heated in the wash-heater sufficiently to form vapour this passes into the small dephlegmator, *H*, whence the condensed alcohol and water are led by the tube *S r* to the column, whilst the alcohol vapour which is not condensed proceeds through *t* to the condenser along with the other alcohol. When all the plates of the column are covered with wash, steam is passed in from below by heating the exhausted vinasse by pipes from the heater, *G*, in which superheated steam from suitable boilers circulates; this steam is regulated by the tap *j*, which in its turn is controlled by the automatic regulator *F*. When the distilled alcohol issues from the test-glass, *E*, the access of wash through 2 is regulated so that the alcoholic strength remains constant. In the column the wash traverses a path more than 125 metres in length, the total absorptive surface being more than 200 metres, so that every litre of wash, before exhaustion, meets a surface of vapour 200 metres long. In this way 30,000 kilos or more of wash can be distilled per day without interruption of the working for months.

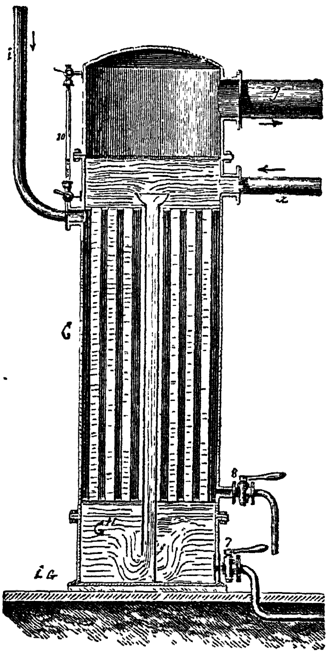


FIG. 130.

Fig. 130 shows Savalle's tubular heater more in detail. Steam under pressure from ordinary boilers traverses the regulator, *E*, and passes through the tube *i* to a large metallic cylinder, *G*, which contains a series of vertical tubes connecting the upper chamber, *G'*, with the lower one, *G''*; the latter is filled with almost exhausted vinasse supplied from the lower part of the Savalle column by the pipe *x*. The spent wash, which is already very hot, is thus easily brought into a condition of vigorous ebullition and loses the last traces of alcohol, which rise with a large quantity of steam through the pipe *y* into the Savalle column. The exhausted spent wash is discharged continuously from the tube 7, whilst the condensed steam issues from the tap 8.

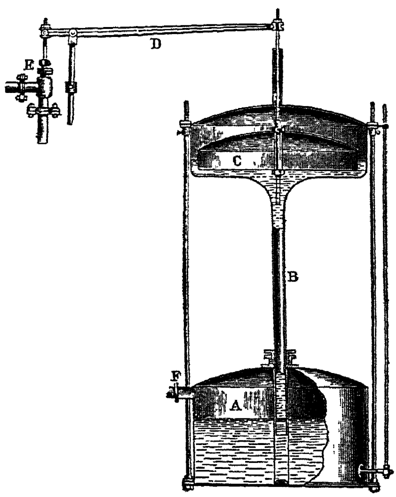


FIG. 131.

Fig. 131 shows the *automatic regulator of the pressure* and steam in the distillation and rectifying column. In order that it may pass through all the layers of liquid on the plates of the column the steam must be at a certain pressure in the column itself; this pressure increases or diminishes according as the quantity and temperature of the steam rise or fall, and the greater the supply of steam the more dilute will be the alcohol. If the column is connected with the pressure regulator by means of the tube *F* (*f* in Fig. 129),

then, when the pressure increases, the water in the lower chamber, *A*, of the regulator is forced along the tube *B* to the upper chamber and raises a float, *C*, which operates the lever *D*, and so partially closes the tap (or valve) *E* controlling the supply of steam to the heater, *G*; owing to the diminished supply of steam the pressure falls. In the opposite case, when the pressure in the column is smaller than that necessary for regular distillation, so that the concentration of the alcohol (measured in *E*, Figs. 129 and 132) becomes too high and the yield too small, the water of the upper chamber of the regulator descends to the lower one, the float, *C*, hence falling and the steam-cock, *E*, opening a little. With these regulators, which are sensitive to variations of one-thousandth part of an atmosphere, the distillation is automatically regulated and requires very little personal control.

The constancy of the strength of the alcoholic distillate is controlled by the test-glass, *E* (*see* Fig. 132), which is situated in the alcohol discharge tube and contains an alcoholometer fitted with a thermometer, so that the concentration and temperature are indicated continuously.

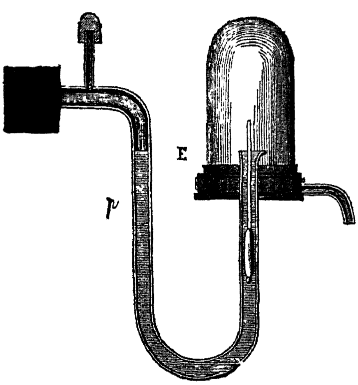


FIG. 132.

Of the variously highly perfected forms of apparatus (Ilgès, Coffey, Pampe, the last of which gives very pure spirit by distillation under reduced pressure) used in England, Germany, Russia, &c., which allow of the continuous and direct production of 90 to 96 per cent. alcohol without special rectification and refining (when the first and last products of distillation—*foreshots* and *tailings*—are kept separate; *see later*), we shall refer only to the apparatus of Siemens Brothers, which is largely used in Germany (Fig. 133). The column is composed of three principal parts: the heater (or pre-heater), *A*, the distillation column, *B*, and the rectifier, *C*; the whole is formed of superposed cast-iron discs or rings fitted with pasteboard packing and held tightly together by bolts extending from the top to the bottom. Inside are plates arranged spirally round a central tube, *D*, which passes about half-way up the column to *f*; the liquids thus traverse a long path, so that a large production is possible with a relatively small tower-space. The apparatus is also economical since it is not necessary to construct it of copper. The heater, *A* (*see also* Fig. 134, *A*), contains, in the chambers *a* and *o*, hot spent wash which comes from the top of the column. Between these hot chambers are arranged alternately others in which circulates the cold wash or wine to be distilled; this is supplied through the pipe *d* by means of high-pressure pumps, and begins to be heated as it descends the spiral chambers between the hot ones containing the spent wash. When it reaches the bottom the hot wash passes into the central pipe *D*, and rises to the higher level, *f*, in the distillation column, *B* (which embraces the space between *d* and *E*). The pipe *D* empties on to the perforated spiral plates (*see* Fig. 134, *B*) and, as it descends, the wash meets a current of steam rising from the tube *o* through *B*. In this way the alcohol liberated from the wash rises with the steam through the perforations of the spiral plates and thus continually meets fresh quantities of wash and becomes continually richer in alcohol, as is shown in Fig. 134, *B*. The wash, thus deprived of alcohol, reaches the bottom as very hot spent wash, which, before leaving the column, traverses the chambers of the heater (shown in Fig. 134, *A*) and is then discharged continuously from the pipe *J K*, at a lower level than *f*. The mixed alcohol and water vapours enter the rectifying compartment, *E*,[1] which is formed of plain discs and is filled with wash, the level of which can be seen through suitable glass windows. The alcohol vapours rise into the rectifier, *C* (more properly termed a *fractionator* or *dephlegmator*, *see* p. 133), formed of non-perforated and hence non-communicating spiral chambers (Fig. 134, *C*), in some of which circulate the ascending vaporous mixture, whilst the alternate ones are traversed by a descending current of water; the latter is not very cold, as it comes from the top of the condenser, *S* (by means of the pipe *t*), so that it condenses mainly steam and only a little alcohol vapour,

[1] Pampe (Ger. Pat. 199,142, 1908) suggests placing, before the rectifying compartment, a steam-turbine with rapidly rotating vanes, which separate all the suspended drops or impurities from the vapours.

which falls into the distilling column again. The alcohol vapours gradually become more and more highly concentrated and pass through the tube *F* to the refrigerator, *S*, where they condense and are cooled by water flowing in at *s* and out at *t*. By means of a sample taken from the column *B* by the tube *p* and examined in the tester, *T*, it can be ascertained if the spent wash is completely free from alcohol.

In some cases it is observed that the spirit from such a cast-iron apparatus absorbs traces of hydrocarbons and of hydrogen sulphide which are formed

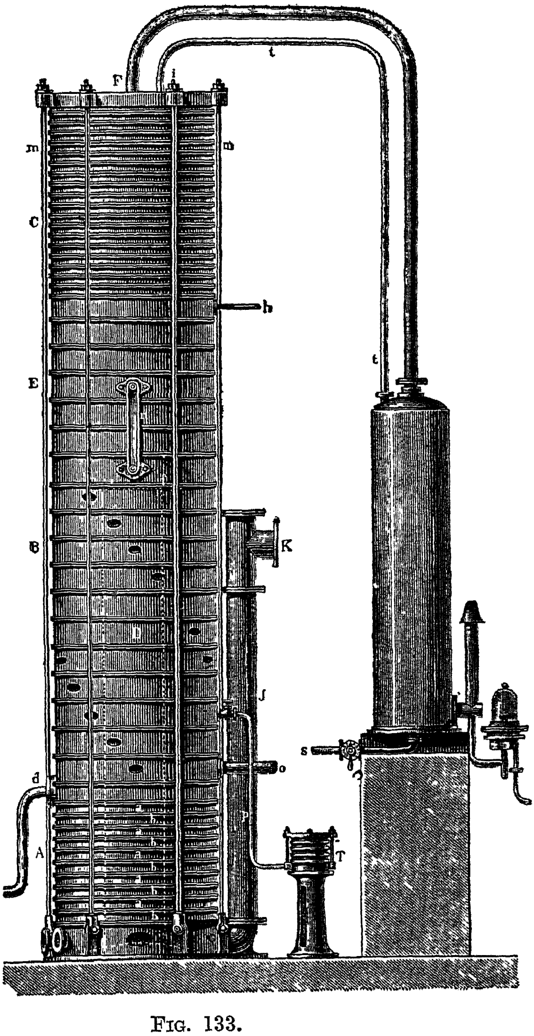


FIG. 133.

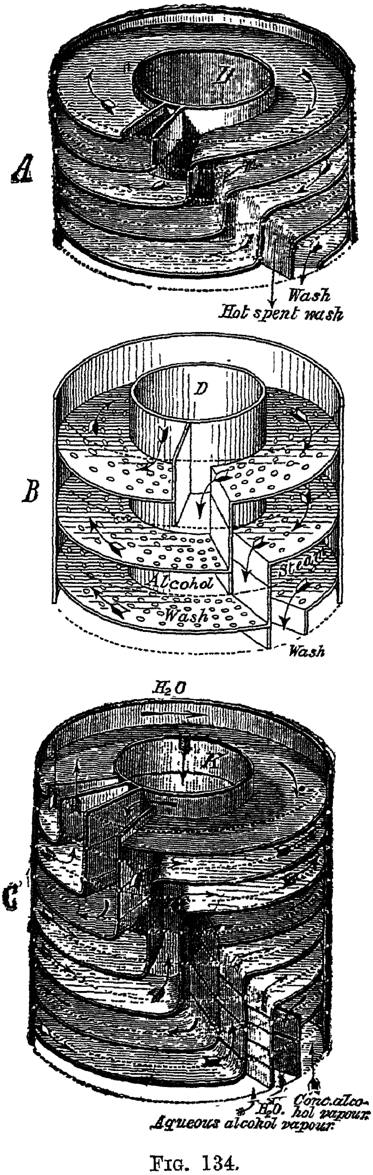


FIG. 134.

from the iron and give an unpleasant taste and smell to the alcohol; this may, perhaps, depend on the quality of the metal and on the newness of the apparatus.

We shall mention finally the attempts which have been made, first by Perrier in 1875, to transform the vertical column into a horizontal distilling and rectifying column with a central rotating axis carrying helically arranged blades, which transport even a very dense wash from one end to the other, whilst the opposing current of steam removes the whole of the alcohol. The process was perfected by Sorel and Savalle (1891), who arranged the numerous vertical chambers of the horizontal column in a more rational manner. These forms are not yet free from disadvantages, but they have the advantage of being

considerably more economical to construct and of bringing all the taps conveniently to hand on the same level.

Lastly, Guillaume eliminated various defects of these columns and at the same time retained all their advantages by employing very simple and convenient inclined columns (made by Égrot, of Paris), which allow of very dense washes being employed without danger of obstruction. Fig. 135 shows the complete Guillaume-Égrot apparatus, and the description of the various parts given underneath will indicate the way in which it works. The cross-section shown in Fig. 136 gives an idea of the internal arrangement of the inclined column, and Fig. 137 represents the ground plan of the column, the arrows indicating the horizontal, zigzag course followed by the liquid from the highest part of the column, whilst the vapours ascend the column in a zigzag vertical path and bubble through the liquid in all the chambers formed by the numerous vertical partitions. With relatively small plant, which can be mounted on portable cars (*see later*), 30,000 litres or

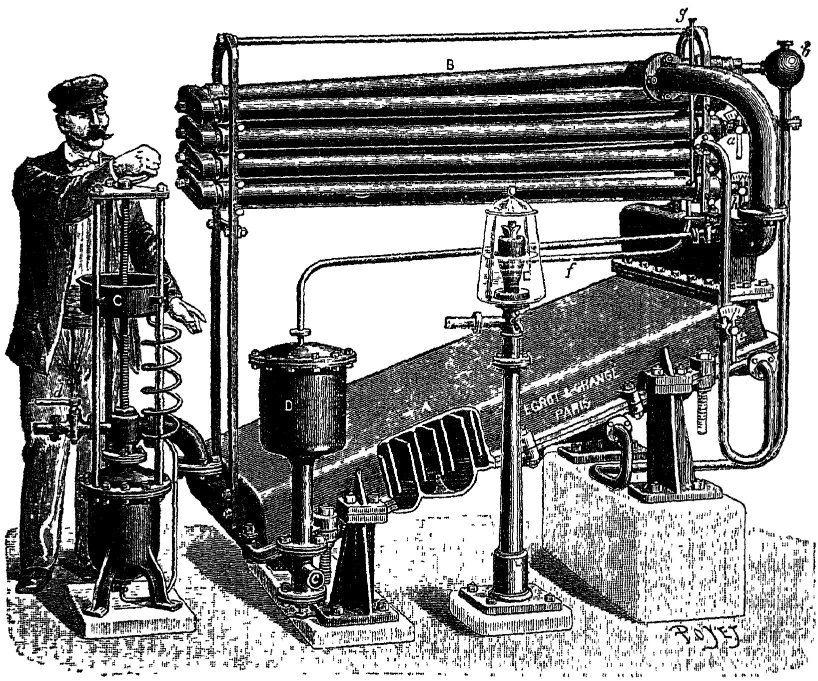


FIG. 135.

A, distilling column; *a*, entrance of the wash into the heater or refrigerator; *B*, condenser and heater; *b*, hot wash pipe; *C*, adjustable steam regulator; *c*, exit for spent wash; *D*, hot wash extractor used as heater; *d*, steam-tap; *E*, test-glass giving the strength of the alcohol; *e*, valve regulating flow and hence strength of the alcohol; *h*, entrance of water into refrigerators in case of need.

more of wash, containing 10 per cent. of alcohol, can be distilled per 24 hours, 90 per cent. alcohol being produced.

In the modern distillery the consumption of steam should not exceed 25 kilos (about 3 kilos of coal) per 100 kilos of wash, and the consumption of water in the condenser should not exceed 80 litres.

RECTIFICATION OF ALCOHOL. The alcohol obtained with the ordinary Savalle apparatus is not sufficiently concentrated or pure to be placed on the market, and even that obtained with other forms from washes which have not been fermented with selected yeasts should be freed by rectification and refining from various impurities which impair the colour, smell, and taste. These impurities may be more volatile than alcohol (such as aldehydes and certain esters) or less volatile (as acetic and butyric acids; propyl, isopropyl, and amyl alcohols; various esters, &c.), and they are separated from the *true alcohol* if, in the redistillation and rectification, the portions which distil most readily (*foreshots*) and also the least volatile portions (*tailings* or *fusel oil*, which has a very

disagreeable odour if obtained from potatoes, molasses, or maize, but a pleasing odour if derived from grapes, fruit, &c.) are kept apart.

Rectification apparatus usually consists of a large copper or iron boiler, *A* (Fig. 138), which is heated with an indirect steam-coil and on which is mounted the copper rectifying column, *B*. Above this and to one side is a large dephlegmator, *C*, which serves as a heater, and is of importance not so much for condensing the less volatile products (water, amyl alcohol, &c.) as for furnishing a continuous and abundant supply of a suitable alcoholic liquid to wash the vapours arriving at the top of the column; it is, however, quite useless to employ several dephlegmators, as was erroneously done in the past. The foreshots, which have a concentration up to 94 per cent. and boil at 85°, are collected separately. Then from 85° to 102° alcohol passes over. The tailings, boiling above 102°, are collected in the bottom of the column by shutting off the steam and thus emptying the plates. The quantities of these products vary according to the quality of the alcohol required; thus 20 per cent. of foreshots and tailings may be obtained and 80 per cent. of alcohol (*bon goût* extra), or 5 per cent. of foreshots and tailings and 95 per cent. of alcohol (*bon goût*).

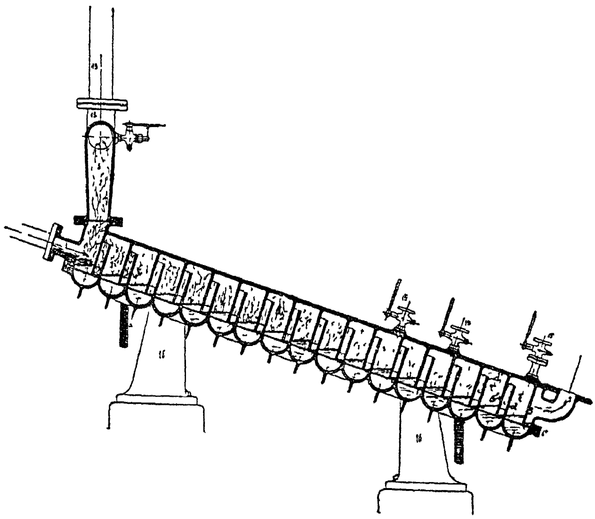


FIG. 136.

This apparatus does not work continuously, the boiler requiring to be discharged and recharged. Attempts to render the process continuous were met with success in 1881 (E. Barbet) in spite of the difficulty of separating the pure alcohol from an impure product that boils below it and another that boils above it. This is effected by carrying out the operation in two phases, which are, however, continuous; in the first phase the foreshots are driven off and the alcohol distilled from the remaining liquid, the tailings being left behind. The boiler is then replaced by a rectifying column, which receives the impure product and distils the foreshots, passing the residue continuously at a certain height to a second lower column at the side; this distils and rectifies the pure alcohol and retains in the lowest chamber of the column the tailings, which are continuously discharged.

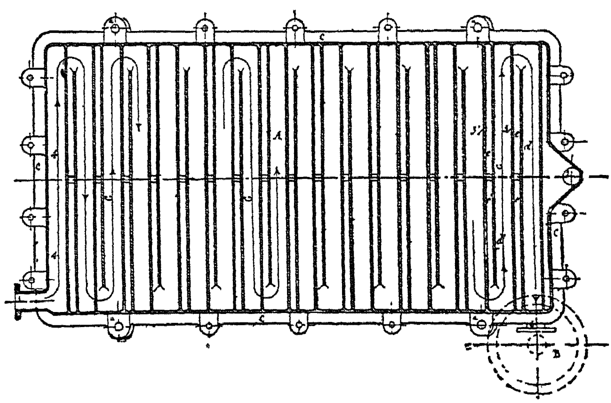


FIG. 137.

In the Savalle rectifiers 45 kilos of coal are consumed per hectolitre of pure rectified alcohol. Continuous rectification results in a saving of almost 50 per cent. of fuel compared with the discontinuous process. During rectification the loss of alcohol is 1 to 2 per cent., and the cost of rectification varies from 3 to 3·5 lire (2*s*. 6*d*. to 3*s*.) per hectolitre. The firm of Savalle holds that it is more economical to use cold air than water in the refrigerators of the condensers.

Attention may lastly be drawn to the ingenious although complicated Perrier distilling and rectifying apparatus, in which the vapours of alcohol, water, higher alcohols, and aldehydes are passed successively into columns filled with glass beads and surrounded by a jacket containing a liquid boiling at a constant temperature, the latter being hence assumed by the whole of the tower. In one of these, having a temperature of 85 to 90°, only water and the tailings are condensed; the vapours then pass into a second tower, kept at 75°, where all the ethyl alcohol (which can be rectified in another tower) separates; the vapours from this form the foreshots and are condensed in a succeeding tower.

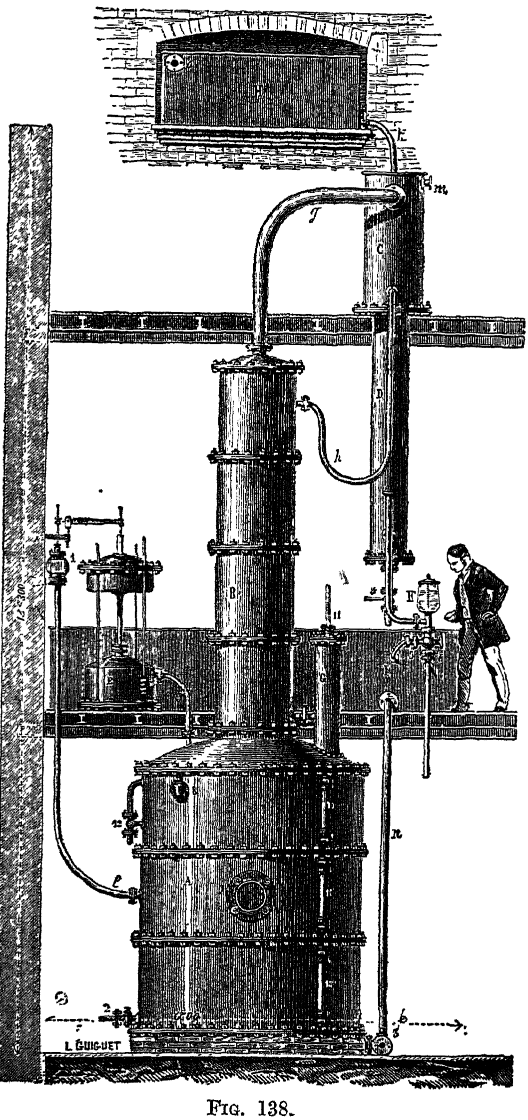


FIG. 138.

OTHER PRIME MATERIALS FOR THE MANUFACTURE OF ALCOHOL. (1) **Beetroot** and **Molasses.** It is especially in France that considerable quantities of beet are used for the manufacture of alcohol instead of sugar; this is never done in Germany or Italy. The beets are washed, minced, and the pulp exhausted by pressure, maceration, or diffusion with water. This treatment is described in the section on *sugar*.

The spirit obtained from the beet is less pure than that from potatoes, containing more propyl and butyl alcohols but less amyl alcohol.

Of more importance in Italy and various other countries is the utilisation of *beet-molasses*.[1]

The complete fermentation of molasses has presented many difficulties, which have now been overcome. Formerly, after the molasses was diluted to 8° to 10° Bé. (this was carried out in vats provided with stirrers, *see* Fig. 139), it was slightly acidified with sulphuric acid (2·5 grms. of free H_2SO_4 per litre), as the reaction is usually alkaline. The liquid was then boiled for some

[1] These are the dense, viscous, and blackish mother-liquors which remain from the final crystallisation of the sugar (*which see*) and from which no further sugar will crystallise although 45 to 50 per cent. are present (*see* explanation in the section on Sugar); it has a density of 40° to 45° Bé. (74° to 84° Balling). The composition of beet-molasses is as follows: water, 16 to 20 per cent.; sugar, 44 to 52 per cent; non-nitrogenous extractive matters, 10 to 15 per cent. (largely pentoses); nitrogenous compounds, 6 5 to 9·5 per cent (of which only one-third consists of proteins, the rest being amino-acids); ash (deducting CO_2), 8 5 to 11 per cent. In Italy the working-up of molasses has assumed considerable importance during the last few years, owing to a change in the method of taxing sugar; previous to 1903, sugar recovered from molasses by somewhat expensive processes (*see* Sugar) was exempt from taxation, whilst nowadays all sugar produced is taxed uniformly, so that the manufacturers find it advantageous to sell the molasses to the distillery at 4*s*. 9*d*. to 6*s*. 5*d*. per quintal.

In Germany, Belgium, and part of France, it is found to be more convenient and rational to utilise a large proportion of the molasses as cattle-food after absorbing it by highly porous vegetable substances. In Italy, *tumelina*, patented by E Molinari, and *sanguemelassa* (blood-molasses), patented by L. Fino, are manufactured; the residues of dried tomatoes (Squassi, Bono) and various other dried industrial products are now used as absorbents. In Germany more than 1,500,000 quintals of *molassic fodder* are consumed; Italy produced 400,000 quintals in 1908 and more than 480,000 in 1909.

hours in a current of air in order to eliminate the volatile acids (nitric, &c.) liberated, and, after cooling it to 15°, alcoholic fermentation was initiated by the addition of vigorously fermenting liquid; the excess of acid which forms is gradually neutralised with chalk. The spirit thus obtained is difficult to purify as it contains an aldehyde and various acids which boil at a very low temperature.

To-day, however, the process is much more simple, as Jacquemin and Effront have devised various methods of preparing races of yeast capable of living actively in worts rich in salts (nitrates, carbonates, &c.), such as those prepared from beet-molasses. In the past the difficulty of fermentation was attributed to the presence of nitrates, but it appears from Fernbach and Langenberg's experiments (1910) that nitrates, even in proportions as great as 0·3 per cent., facilitate fermentation.

(*a*) In the Jacquemin process the fermentation is initiated in small quantities of wort in suitable vessels (*see* Fig. 123, p. 125), and the wort of the last rather larger vessel (into which is also placed a little hydrofluoric acid, to which the yeast has been previously "acclimatised") serves to pitch a 200-hectol. vat containing diluted, non-sterilised molasses, to which has been added 8 to 10 kilos of calcium hypochlorite, this preventing the development of heterogeneous organisms during the first few hours without damaging the yeast—already adapted to chlorine. By means of this vat two other 500-hectol. vats of similar diluted molasses can be brought into a state of vigorous fermentation; the fermentation takes place so rapidly (and this is the most specific action of these yeasts) that in three days the whole of the molasses is fermented, there being thus no time for the development of extraneous germs causing harmful secondary fermentations.

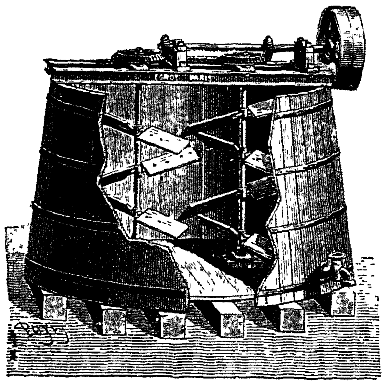


FIG. 139.

(*b*) The Effront process is still more simple, and is based on the use of selected yeasts specially adapted to molasses worts and endowed with exceptionally rapid fermenting properties; these yeasts are placed under such conditions that they easily overcome deleterious bacteria (namely, the addition of resin) [1] and complete the fermentation before these become harmful. To the molasses simply diluted with water and not sterilised are added these special yeasts together with 1 kilo of colophony per 10 hectols. of wort; in three days the fermentation is complete. In 1903 almost 1,000,000 kilos of colophony were used in France for this purpose.

(2) **Alcohol from Fruit.** This is not of great industrial importance, although in certain districts and in certain years it assumes considerable magnitude. In Italy, dried figs of little commercial value, carobs, &c., are used; and, in other countries, plums, apples, pears, &c. These fruits often give an irregular, and seldom a complete, fermentation, owing to conditions similar to those encountered with beet-molasses. Hence, as in the latter case, use is made of very active yeasts adapted, where possible, to these special worts.

The alcohol obtained from these worts has a characteristic odour indicating its origin.

[1] Effront observed that the *law of the strongest*, which is often verified in bacteriology—the most numerous and powerful bacteria rendering life impossible to weaker ones—scarcely ever holds in the case of alcoholic fermentation, where, even though the harmful bacteria are less numerous than the yeasts, the latter are seldom victorious, the bacteria often entirely arresting alcoholic fermentation even when the conditions are favourable for the latter.

According to Effront, this is owing to the different specific gravities possessed by yeasts and bacteria, which hence live in different, relatively distant strata, so that there is no opportunity for the application of the law of the strongest—which consists in the production by certain micro-organisms of poisonous substances preventing other forms from developing. Effront hence proposes to add suitably emulsified resin (colophony) to the worts at the beginning of the fermentation; this has the property of coagulating only the bacteria, which become denser and are brought into more intimate contact with the yeast, the latter then being in the most favourable condition for the annihilation of the bacteria. The resin itself is not the cause of the death of the bacteria, as Effront states that these can be readily cultivated in the pure state in presence of resin (private communication).

(3) **Alcohol from Woody Substances.** This is a subject which has aroused considerable interest during about the last twenty years. Many attempts have been made to transform a part of the wood (sawdust, peat, &c.) into fermentable sugar by the action of acids on the matter (lignin) encrusting the wood and not on the cellulose. In Chicago the process was applied on a vast industrial scale according to A. Classen's patents (Ger. Pats. 130,980, 1899, and 161,644, 1904). 100 kilos of wood (with 25 per cent. of moisture) are treated in an autoclave for an hour with about 100 kilos of aqueous sulphur dioxide and sulphuric acid in presence of steam at 6 to 7 atmos. pressure (150° to 165°). The excess of sulphur dioxide is eliminated by means of a current of air, the residue being boiled with water or extracted in diffusers, and the liquid neutralised with calcium carbonate and fermented;[1] about 8 litres of pure alcohol are thus obtainable, and the residues are partially utilisable for making paper. It is not improbable that in the near future wood and the more economical wood refuse will replace cereals and potatoes in spirit factories.[2] In France, England, and the United States there were in 1910 four factories making alcohol from wood and obtaining yields of 7 per cent.

(4) **Alcohol from Wine, Lees, Vinasse, and Withered Grapes.** In seasons when

[1] Wood thus yields a product containing 35·36 per cent. of solid residue, 34·63 per cent. of water, 10·97 per cent. of fermentable reducing sugar, 3·21 per cent. of non-fermentable reducing sugars (pentoses: xylose, &c.), 0·35 per cent. of sulphuric acid, and 0·77 per cent. of other acids.

[2] As early as 1820, Braconnot observed that sugar is formed when wood or even cotton cloth is treated with sulphuric acid. Later on Melsens obtained a good yield by treating cellulose with dilute sulphuric acid in an autoclave under pressure. In 1860 Pettenkofer investigated this process and showed that it could, at that time, compete with the use of potatoes. Still later, Basset prophesied a yield of 32 per cent of alcohol from the similar treatment of wood (!). Simonson, in 1889, treated wood under pressure with dilute sulphuric acid, transforming 25 per cent. of it into sugar (78 per cent. of which was fermentable) and obtaining a practical yield of 6 to 7 litres of pure alcohol (Third International Congress of Applied Chemistry, Berlin, 1903).

Reiferscheidt (1905) overcame the resistance of the wood to penetration by liquid acid (met with also by Classen) by causing sawdust to absorb two-thirds of its weight of sulphuric acid (sp. gr. 1·65) and subjecting the mass to the maximum pressure of a hydraulic press; simple digestion of the mass with water and filtration gave a fermentable liquid and a yield of 6 5 per cent. of alcohol on the weight of wood (pine, containing 53 per cent. of cellulose) taken. A similar yield is obtained by treating the wood with five times its weight of 1 per cent. sulphuric acid solution at a pressure of 8 atmos. for fifteen minutes. He confirmed the observation that the pentosans of the wood do not ferment, and with pure cotton he obtained as much as 13 per cent of alcohol.

According to Th. Korner, the addition of oxidising agents or of ozone, as was suggested by Roth and Gentzen (1905), is of no advantage. He obtained the best yields by heating sawdust, straw, &c., with 0 5 per cent. sulphuric acid for 2 hours in an autoclave at 6 to 8 atmos; only a small part of the molecular complex of the cellulose is converted into fermentable sugar, and he obtained a yield of alcohol equal to 15 to 18 per cent of the weight of the true cellulose in the wood. Without the addition of sulphuric acid, the yield was about one-fourth less.

F. Ewen and H. Tomlinson, of Chicago (U.S. Pat, 938,308, 1909) treated 400 kilos of sawdust, straw, or stems of various cereals (with 30 per cent. of moisture) in autoclaves with 5 kilos of sulphuric acid of 60° Bé. diluted with 20 litres of water; after complete digestion and agitation the temperature of the mass is brought in fifteen minutes to 135° to 160° by means of steam under pressure; after half an hour the temperature is lowered rapidly to 100° by allowing the steam to escape, and the sulphuric acid then separated in the usual way. By this means 20 to 30 per cent of the weight of the cellulose is transformed into fermentable sugar. A similar process is that of Eckström (Norw. Pat. 17,634, 1907).

Classen's process, which has been tried on a large scale in North America, has exhibited various disadvantages: the time required for treating 2 tons of wood was as much as six hours, the consumption of sulphuric acid was large, part of the sugar was destroyed, and frequent repairs were necessary. The process was improved by Ewen and Tomlinson, and was worked in a factory near Chicago. Less acid was used and the treatment maintained only for forty minutes, the autoclave being rotatable and made of steel protected outside with fireclay This was filled with sawdust, sulphur dioxide (1 part per 100 of dry wood) being then passed in, and subsequently steam at 7 atmos. After forty minutes, the vapours of water, acetic acid, terpenes, and sulphur dioxide are passed into washing or absorption vessels, while the residual darkened sawdust is extracted with hot water: the aqueous extract is neutralised with chalk, filtered, fermented, and distilled. Rectification yields 94 per cent. alcohol free from methyl and higher alcohols, and containing only traces of furfural and other aldehydes, The cost of this alcohol seems to be less than three-halfpence per litre of 90 per cent. concentration.

J. Ville and W. Mestrezat (1910) state that, whilst cellulose resists dilute solutions (up to 30 per cent.) of hydrofluoric acid, with 50 per cent. solutions, 100 grms. of cellulose yield 50 grms. of glucose!

According to the Swedish patents of J. H. Vallin and of Eckström, alcohol is obtained by treating the *waste sulphite liquors of paper-mills* in the hot with sulphuric acid and fermenting the liquid containing the glucose formed. The hot acid liquid has to be neutralised *almost* completely with chalk and decanted, the residue being then pressed in a filter-press; the liquid is then cooled on piles to 30°, pitched with yeast, aerated during fermentation (5 to 6 hours) and the dilute alcoholic liquid (0·7 to 0 8 per cent alcohol) distilled. From 10 cu. metres of the sulphite liquors are obtained 60 litres of 100 per cent. alcohol (which is, however, of bad flavour and is used for denaturation). For a factory producing 60 tons of cellulose per day, *i e.* 600 tons of waste sulphite liquors, the cost of tanks, pumps, piles, distilling apparatus, filter-presses, &c., may be taken as about £6000, and the alcohol produced (36 hectols. per day) would cost (including all expenses, but excluding taxation) 10*s.* to 11*s.* per hectolitre at 100 per cent. strength. The problem of the disposal of the waste liquors (which contaminate the rivers) of paper-mills is not, however, solved in this way, since the liquid still contains much decomposable organic matter after the distillation of the alcohol. Before starting such an industry, it is also necessary to consider the condition of the market, so that there may not be an over-production of alcohol and hence depression of prices.

In 1910 there were two factories in Sweden for the manufacture of alcohol from these *waste sulphite liquors*: that at Billingfors prepared *methyl alcohol* (15 kilos per ton of wood pulp) by H. Bergstrom and H. Fahl's process; the other at Skutskür manufactured ethyl alcohol. For every ton of cellulose there are obtained 8 to 9 tons of

wine is abundant and prices low and in general when there are spoilt wines (at 6*s.* to 8*s.* per hectolitre), it is convenient to extract the alcohol from them, this being of use in the preparation of liqueurs and spirits.

The distillation presents no difficulty and is carried out either in the large distilleries or with a Guillaume-Égrot apparatus (*see* p. 138), which is mounted on a car so as to be readily transportable, and can be used in places where there is little available water, since the coolers and condensers act as heaters and are fed with the wine to be distilled. It gives directly 90 to 94 per cent. alcohol.

In the same way as wine, fresh lees or bottoms from wine vats (containing 4 to 6 per cent. of alcohol) and *dried grapes* [1] are treated.

The distillation of *vinasse*, containing 2·25 to 3·5 per cent. of alcohol, is of considerable importance in Italy; if this were all distilled it would yield about 250,000 hectols. of pure alcohol annually (for a production of 40 million hectols. of wine). Of the various forms of apparatus for the distillation of vinasse only those of Villard-Rottner and of Égrot will be described, as they are the commonest and differ little from other good types.

The generator, *K* (Fig. 140), of the Villard-Rottner apparatus sends steam from the dome, *M*, into the three boilers, *A*, in succession, the steam entering at the bottom and

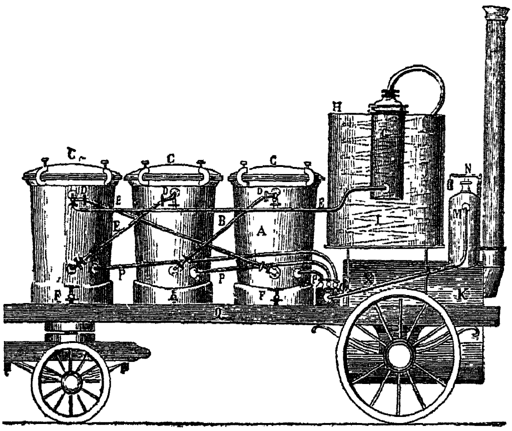


FIG. 140.

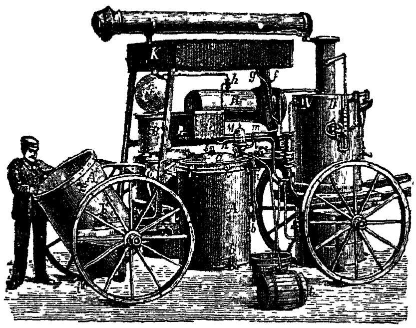


FIG. 141.

issuing at the top of each. These three boilers contain the vinasse mixed with an equal volume of water. The vapours, which are rich in alcohol, pass through the pipe, *E*, to the dephlegmator, *G*, and are then condensed in the coil, *I*, at a concentration little exceeding 50 per cent. When the first boiler is exhausted it is emptied and again charged, the steam passing meanwhile through the second and third; the first boiler now becomes the third, the second being then emptied, so that two boilers are always in use. The hot water from the boilers is treated separately for the extraction of tartar (*see this*).

In the Égrot apparatus (Fig. 141) the boilers, *A*, are arranged on pivots, so that they

sulphite liquors containing, either dissolved or suspended, as much as 12 per cent. of organic substances and yielding alcohol at less than 1½*d.* per litre.

Considerable interest was aroused in 1901 by the English patent of Dornig and Prätorius, according to which *human fæces* yielded about 9 per cent. of alcohol, but it proved to be a fraud.

There has been much discussion recently (1906–1907) concerning a process for extracting spirit from *peat* in a manner similar to that described for wood. These attempts date from 1870, and various patents were filed in 1882–1891. The most important tests were made in Norway in 1906 by the Reynaud process (1903), in which 300 kilos of peat were treated in the hot with 700 kilos of water containing 7 kilos of sulphuric acid (66° Bé) under 3 atmos pressure; 600 litres of liquid were thus obtained and this was fermented with specially selected yeasts (*Saccharomyces ellipsoideus*), the yield being 25 litres of burning spirit at an inclusive cost of about 4·5*d.* per litre, which is about double the cost of that obtained from ordinary starchy materials. In 1905, the Danish Government offered a prize for the improvement of this process, but the yield was not increased although it varies somewhat (6 to 8 per cent.) with the quality of the peat; in all cases the alcohol obtained in this way is too costly.

[1] In some countries—at certain times in Italy—dried grapes are used for the production of alcohol, especially Greek grapes, which are received from viticulturists by the Greek Government in payment of taxes, and are dried and placed on the European markets. These grapes are first macerated in tepid water, then crushed and fermented in the usual way; the *wine* obtained may be used for mixing with other wines or for distillation. In 1905–1907, in order to help the crisis in the South, the Italian Government granted a considerable rebatement of taxation on the alcohol obtained from grapes The Italian distillers then began to import large quantities of Greek grapes (containing 50 to 55 per cent. of sugar), which could be delivered in the factory at about 13*s.* per quintal, so that the southern viticulturists reaped no advantage from the rebate, which was hence abolished.

can be inverted and rapidly emptied. Steam from the boiler, *D*, extracts the alcohol from the three boilers, which are arranged in series, as before, so that two are always in use while the third is being emptied and recharged. The alcohol vapours pass into the dephlegmator, *B*, and thence into the spherical rectifier, *C*; *R* acts as a condenser and is cooled by water from the tank, *K*. The condensed alcohol passes along the tube, *m*, to the test-glass, *M*, and from there to the casks, *t*, at a concentration of 55 to 60 per cent.

With the first apparatus, to treat 100 quintals of vinasse, yielding about 8 hectols. of brandy at 51 per cent., roughly 13 quintals of coal are consumed, whilst the Egrot apparatus uses much less than this for an equal yield. The brandy thus obtained has almost always a rather unpleasant flavour and is often used for rectification in the ordinary way (if too dilute it becomes opalescent) and is then left to age in oak casks so as to acquire a pleasing aroma. This result is obtained more rapidly by *pasteurisation*, that is, by passing the brandy through a coil surrounded by water at 60° to 65°, or by passing a current of ozonised air through it (*artificial maturation*). The name *cognac* is given to the finest old French brandies.

Alcohol from cereals can be distinguished from that obtained from wine, &c., as the latter always contains aldehydes (*see later*, Rimini's Reaction and Schiff's Reagent).

REFINING AND PURIFICATION OF SPIRIT. After the introduction of rational methods of fermentation with selected yeasts and of more perfect rectifying appliances, the quantity of *actual alcohol* was considerably increased and it was generally sufficiently pure for ordinary commercial purposes. But when it became recognised that the harmful effects of alcoholism are aggravated by the presence in commercial alcohols for liquors, &c., of even minimal quantities of aldehydes and amyl alcohol, recourse was sometimes had to a special *purification* or *refining* of rectified spirits in order to give them a slight ethereal odour, which is greatly valued. Of the many and varied substances suggested for the purification, mention need only be made of charcoal in lumps calcined and cooled out of contact with air and placed in batteries of tall cylinders through which the alcohol is passed; when the charcoal becomes inactive it is revivified by means of superheated steam at 600°. The charcoal has an oxidising, esterifying, and decolorising action, but it does not fix the amyl alcohol. Treatment with fatty oils (which retain the aldehydes) and subsequent distillation are also used, as also are carbonates of the alkalis and alkaline earths. Treatment with oxidising agents—ozonised air, potassium permanganate or dichromate, nitric acid, chloride of lime, &c.—has the disadvantage of forming acetic acid and ethyl acetate. Consequently Naudin prefers reducing the aldehydes with nascent hydrogen formed in the liquid itself by means of a copper-zinc couple.

R. Pictet has devised a totally different process: owing to the variations (at different temperatures) of the maximum vapour pressure of volatile liquids, he ascertained that the vapours obtained from a mixture of water or other substances with alcohol are the richer in alcohol the lower the temperature to which the mixture is heated. He boils the mixture at 50° to 60° in a vacuum and then rectifies the vapours in a column at a temperature of $-30°$ or $-40°$, obtained by means of a sulphur dioxide refrigerating machine. The apparatus is somewhat complex, but it yields a well-refined pure spirit.

TESTS FOR THE PURITY OF ALCOHOL. The tests mentioned on p. 109 will detect traces of water in so-called *absolute* alcohol.

If alcohol is highly purified (*puriss.*), 10 c.c. of it, mixed with 1 c.c. of water and 1 c.c. of 0·1 per cent. potassium permanganate solution, should maintain its red colour for 20 minutes, or for at least five minutes if the alcohol is termed *pure*; it should not become turbid on dilution with water, should give neither an acid nor an alkaline reaction (with phenolphthalein), and should remain unchanged with ammoniacal silver nitrate solution. To test for aldehydes the alcohol is diluted with water and a few drops distilled and tested by Rimini's reaction (*see* p. 109); or, for aldehydes in general, by Schiff's reagent(fuchsine solution decolorised with sulphur dioxide: 0·5 grm. of fuchsine is dissolved in 500 c.c. of water and decolorised with 10 c.c. of sodium hydrogen sulphite solution of sp. gr. 1·26 and 10 c.c. of concentrated HCl); a few c.c. of this reagent are coloured red when shaken with a few drops of alcohol containing traces of aldehydes.

Of more importance is the quantitative estimation of the *fusel oil* [1] (always formed in

[1] *Fusel oil* has a varying composition: 14–24 per cent. of water, 15–45 per cent. of ethyl alcohol, 6–14 per cent. of normal propyl alcohol, 10–25 per cent. of isobutyl alcohol, and 10–40 per cent. of amyl alcohol of fermentation. Traces of *fusel oil* may be detected by Kamarowsky's reaction, *i.e.* with salicylic aldehyde and

alcoholic fermentation), which is made with Herzfeld and Windisch's modification of Rose's apparatus (Fig. 142); the method is based on the property possessed by chloroform of dissolving the higher alcohols and a very little ethyl alcohol, at the same time increasing in volume. The alcohol is first diluted to a concentration of 30 per cent. by volume or, better, to the sp. gr. 0·9656 at 15·5° (*see* Table, p. 148; if the alcohol has a concentration, v, less than 30 per cent., then $10(30-v)$ 7 c.c. of absolute alcohol should be added). The Röse tube (washed with alkali, acid, water, alcohol, and ether and well dried) has a cylindrical expansion at the bottom containing 20 c.c. up to the first mark; then comes a tube 18 cm. long, holding 2·5 c.c. and graduated in 0·01 c.c.; at the top is a pear-shaped bulb of about 200 c.c. capacity, closed with a ground stopper. The tube is placed in water at 15° and into it are introduced by a long funnel reaching to the lower bulb 20 c.c. of pure chloroform at 15°, and then 100 c.c. of the alcohol diluted to 30 per cent. at 15° and 1 c.c. of sulphuric acid of sp. gr. 1·2857 (38 per cent. H_2SO_4). The tube is then closed, inverted so that all the liquid passes into the pear-shaped bulb, shaken vigorously for a minute (150 shakes) and placed erect in the water-bath at 15°, where it is left for 15 minutes after a rotatory movement has been imparted to the liquid so as to collect the drops of chloroform adhering to the walls. The increased volume of the chloroform is then compared with that obtained in a similar test with pure alcohol of the same concentration. If no blank experiment is made, 1·64 c.c. is subtracted from the increase in volume as being due to the ethyl alcohol dissolved. Each 0·01 c.c. increase in volume of the chloroform corresponds with 0·006634 per cent. by volume of fusel oil. For an alcohol rich in fusel oil which gave a final volume of chloroform of 22·14 c.c. the true increase in volume will be 22·14—1·64−20=0·5 c.c. The percentage, f, of fusel oil by volume on the original alcohol (not on that diluted to 30 per cent.) is calculated by the following formula:

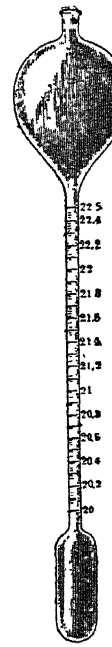


FIG. 142.

$$f = \frac{(c-b)(100+a)}{150},$$

where c is the uncorrected *increase* in volume of the chloroform, b is the correction, 1·64, due to the ethyl alcohol, and a indicates the number of c.c. of water or absolute alcohol added to 100 c.c. of the original spirit to bring it to 30 per cent. *Example:* If 80 per cent. alcohol is used, 171·05 c.c. of water must be added to 100 c.c. to break it down to 30 per cent.; 100 c.c. of this then increases the volume of the chloroform from 20 to 21·94 c.c., so that:

$$f = \frac{(1{\cdot}94-1{\cdot}64)(100+171{\cdot}05)}{150} = 0{\cdot}54 \text{ per cent. by volume of fusel oil.}$$

The *furfural* is determined in 10 c.c. of distilled alcohol, to which are added 10 drops of colourless aniline and 2 c.c. of acetic acid; if a red coloration appears after 20 to 30 minutes furfural is present.[1]

sulphuric acid; H. Kreis's modification (1907) of this colorimetric reaction yields moderately accurate results.

Fusel oil is now largely used for the preparation of amyl alcohol, which is used in the manufacture of fruit essences, for obtaining nitrous and other ethers, and for gelatinising explosives (nitrocellulose); during the last five years the price of fusel oil has risen from 65 to 170, and even 195 lire per quintal. Pasteur thought that the *amyl alcohol* (iso- and d-amyl) arose from the action of specific bacteria on the sugar. But in recent years F. Ehrlich has thrown doubt on the formation of an alcohol with a branched chain from a sugar with a direct chain, and has now shown that it is the proteins of the malt and their decomposition products which furnish nitrogen to the yeast for the synthesis of its protein constituents and at the same time form amyl alcohol. In fact, in the fermentation of a pure sugar, Ehrlich obtained a quantity of fusel oil *proportional* to the quantity of *leucine* added; he was also able to obtain an amount of fusel oil equal to 7 per cent. of the alcohol formed (the usual amount being 0·4 to 0·6 per cent.) and, further, he succeeded in reducing the formation of fusel oil considerably by the addition of ammonium salts. The United States imported 2350 tons (£122,000) of fusel oil in 1910 and 2900 tons (£255,000) in 1911.

[1] The estimation of small quantities of *benzene* in denaturated alcohol can be carried out by means of Röse's apparatus (for more than 1 per cent. of benzene). The best method is to dilute 100 c.c. of the alcohol to a concentration of 24·7 per cent. by weight and to distil the whole; the first 10 c.c. of the well-cooled distillate are diluted to 20 to 25 c.c. with water in a graduated cylinder; the volume of the benzene which separates is increased by 0·3 per cent., which is a constant error of the method. This method of Holde and Winterfeld (1908) is based on the fact that when the alcohol is diluted with water, the pressure of the benzene is considerably augmented, whilst that of the alcohol is diminished.

To ascertain if *methyl alcohol* is present in alcohol, 1 c.c. of it is treated with 1 c.c. of chromic acid solution

ALCOHOL METERS OR MEASURERS. These are important instruments, as in nearly all countries the manufacture of alcohol is subject to taxation which is calculated on the quantity of alcohol passing through a sealed meter indicating automatically the corresponding amount of pure alcohol (100 per cent.). The Siemens measurer is the one most used (Figs. 143 and 144) and somewhat resembles the gas-meter (*see* p. 50) even in its registration. The alcohol, which enters laterally by the tube *l*, is discharged into the inner central part of the drum, *B*, *i.e.* into *D*, this being divided longitudinally into three small chambers furnished with apertures, r^1, r^2, r^3 ; when the small chamber is about half full the alcohol falls into the large lower chamber (*e.g.* *I*), which has a capacity of 4 litres. When this chamber is filled with alcohol the level of the latter reaches the chamber *D*, the alcohol then falling through r^2 into *II* and displacing the equilibrium, so that the drum, *B*, is forced round in the sense of the arrow. At the same time the first 4 litres of alcohol are discharged into the vessel *C*, which communicates with the storage reservoir by means of the tube *G*. The compartment *II* then occupies the position of *I*, and so on. The axis of the drum is connected with a suitable automatic registering device. At the same time, in the cylinder *A* in front of the drum, the alcohol which passes through raises the float, *P*, more or less according to its strength, and a screw, *Q*, operates the lever, *T*, and so moves the index, *S*, the point of which registers the alcoholic strength on a paper ribbon moving along a carefully calculated curve, *X*. In order that alcohols of different concentrations may be well mixed and so influence the float correctly, they are delivered at *E*, where there are two tubes ; one of these, *a*, collecting the lighter alcohol, rises and then descends (*c*), discharging into the bottom of *A* by the perforated tube, *e* ; the denser alcohol passes preferably along *b* and is discharged through the perforated tube, *d*, at the top of *A*, so that mixing is rapid and complete. The registration is also independent of the temperature of the alcohol, as its expansion (or contraction) is allowed for by that of the float.

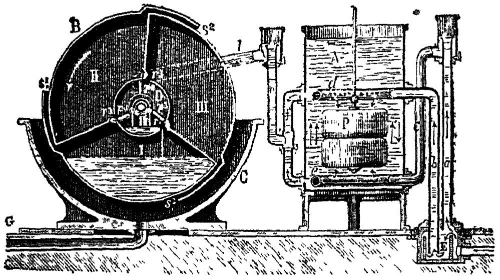


FIG. 143.

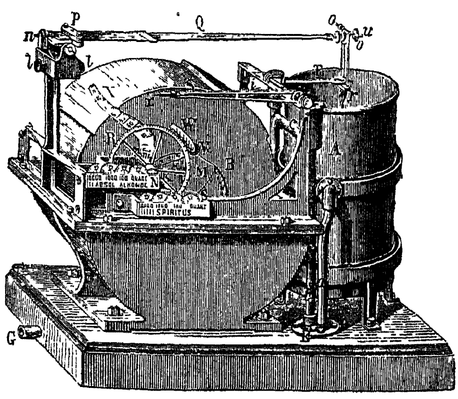


FIG. 144.

ALCOHOLOMETRY AND TESTS FOR ALCOHOL. As a rule alcohol is sold practically by volume and not by weight ; 1 litre of absolute alcohol weighs 0·7937 kilo or 1 kilo measures 1·2694 litre. Industrially alcohol is stated to be of so many *litre-degrees* ; thus 100 litres of 2 per cent. alcohol would contain 200 litre-degrees (100 × 2), and 100 litres of 50 per cent. alcohol would indicate 5000 litre-degrees, which would also be given by 1000 litres of 5 per cent. alcohol ; so also 75·48 litres of 100 per cent. alcohol would be expressed as 7548 litre-degrees. Alcohol is taxed on the basis of the number of litres of absolute alcohol.

The alcohol-content of an aqueous alcoholic solution is deduced from the specific gravity determined by the Westphal *balance*, or directly by the Gay-Lussac *alcoholometer* (at 15°) in France, or by the Tralles *official alcoholometer* (at 15·56°) in Italy and Germany, these giving the percentage of alcohol by volume contained in 100 vols. of the aqueous

and 5 c.c. of water, the whole being then carefully distilled until only 0·5 c.c. remains. The distillate is condensed in a long air-cooled tube and collected in a test-tube, the condenser-tube being washed out with 2 c.c. of distilled water. One drop of ferric chloride and two of albumin solution are added to the test-tube, which is shaken ; 5 c.c. of concentrated sulphuric acid are then cautiously added. The immediate appearance of a violet ring at the zone separating the two layers indicates that the original alcohol contained more than 5 per cent. of methyl alcohol ; if the coloration appears after a minute, the proportion is 1 to 5 per cent. and if after two minutes less than 1 per cent. (A. Vorisek, 1909).

alcohol. The reading on the alcoholometer is made at the point of the stem coincident with the lower meniscus, which is well seen by looking rather below the surface of the liquid (Fig. 145); to avoid error, the alcoholometer must be so immersed that the whole of the graduated stem is not wetted (*see* vol. i, p. 75). To determine the percentage by weight contained in 100 vols. the percentage by volume is multiplied by 0·7937 (specific gravity of absolute alcohol) and divided by the specific gravity of the alcohol examined (*see* Table on p. 148).

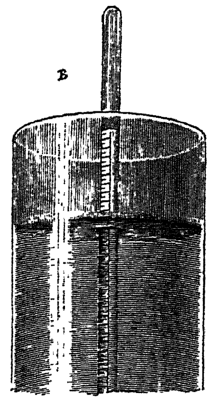


FIG. 145.

To correct the alcohol reading determined at a temperature different from 15° (or 15·56° for the Gay-Lussac alcoholometer), the following moderately exact formula of Francœur is used: $x = c \pm 0{\cdot}39t$, where x is the number of Gay-Lussac degrees at 15°, c the number of degrees found at the non-normal temperature, and t the number of degrees the latter is above or below 15°; the + sign of the formula is used if the temperature is below 15° and the − sign if it is above 15°. Thus an alcohol showing 72° on the Gay-Lussac alcoholometer at a temperature of 28° would have: $x = 72 - 0{\cdot}39 \times 13 = 66{\cdot}93°$ Gay-Lussac at 15°.

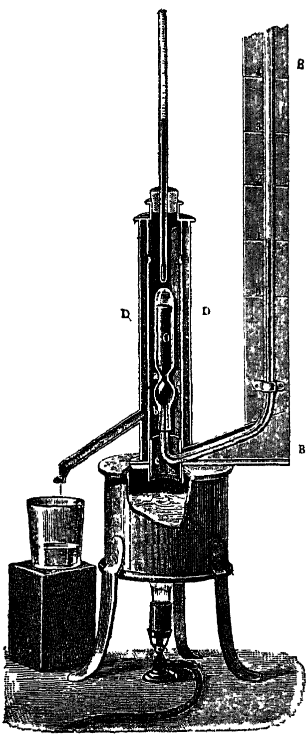


FIG. 146.

With dilute alcoholic liquids of complex composition (wine, beer, spirits, &c.) the alcoholic degrees cannot be deduced from their specific gravities. But, if a given volume, *e.g.* 100 c.c., is taken and distilled (Fig. 147) until all the alcohol has passed over (about 70 c.c.), the distillate can be made up to the original volume with distilled water and its specific gravity and alcoholic strength determined in the usual manner. In order to prevent frothing during the distillation of beer and wine a piece of tannin or a few drops of oil are added. In some cases the alcohol of wines and other liquors is determined by the Geissler *vaporimeter*, which indicates the pressure of the vapours from the liquid heated at 100°. By means of a Table the alcoholic strength may be read off, knowing the vapour pressure; the latter is measured on a special barometric U-tube, *B* (Fig. 146), to one end of which is fixed the bottle, *O*, containing mercury and the alcoholic liquid and placed in the jacketed vessel, *D*, filled with steam from the boiler, *A*. This apparatus gives results which are influenced by several factors (dissolved carbon dioxide, salts, &c.), so that little use is made of it. In more general use is the *ebullioscope* devised in 1823 by Groningen and subsequently improved by Tabarié (1833), Brossard-Vidal (1842), Malligand (1874), Salleron (1880), and Amagat (1885). Malligand's form (Fig. 148) is the most commonly used and is based on the different boiling-points possessed by alcoholic liquids of different concentrations. The reservoir, *F*, is provided with a cover, through which pass a thermometer, *T*, bent at a right-angle and a tube surrounded by the condenser, *R*. This cover is unscrewed and water poured into the reservoir as far as the lowest mark inside, the cover being then screwed on (the bulb of the thermometer does not touch the water). The burner, *L*, is then lighted under the small chamber, *S*, which is traversed by a brass tube communicating with the reservoir; the part *a′* being rather higher than *a*, circulation of

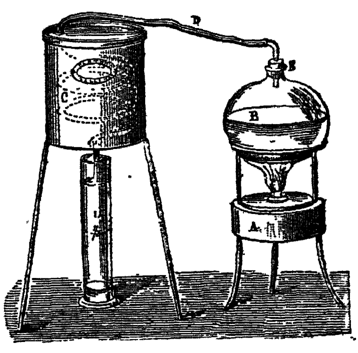


FIG. 147.

WINDISCH'S TABLE FOR CALCULATING THE STRENGTH OF AQUEOUS ALCOHOL SOLUTIONS

Sp. gr. at 15° C.	Grms. of alcohol in 100 grms.	C.c. of alcohol in 100 c.c.	Grms. of alcohol in 100 c.c.	Sp. gr. at 15° C.	Grms. of alcohol in 100 grms.	C.c. of alcohol in 100 c.c.	Grms. of alcohol in 100 c.c.
0·9999	0·05	0·07	0·05	0·9550	31·66	38·06	30·21
0·9992	0·42	0·53	0·42	0·9535	32·55	39 07	31·01
0·9985	0·80	1·00	0·80	0·9520	33·42	40·06	31·79
0·9978	1·17	1·48	1·17	0·9505	34·28	41·02	32·55
0·9970	1·61	2·02	1·60	0·9490	35·11	41·95	33·30
0·9963	2·00	2·51	1·99	0·9470	36·21	43·17	34·26
0·9956	2·39	3·00	2·38	0·9455	37 01	44·06	34·96
0·9949	2·79	3·49	2·77	0·9440	37·80	44·93	35·66
0·9942	3·19	4·00	3·17	0·9420	38·84	46·07	36·56
0·9935	3·60	4·51	3·58	0·9405	39·61	46·90	37·22
0·9928	4·02	5·03	3·99	0·9385	40·62	47·99	38·09
0·9922	4·39	5·48	4·35	0·9365	41·61	49·06	38·93
0·9915	4·81	6·01	4·77	0·9345	42·59	50·11	39·76
0·9909	5·19	6·47	5·14	0·9330	43·31	50·88	40·38
0·9902	5·63	7·02	5·57	0·9305	44·51	52·14	41·38
0·9896	6·02	7·50	5·95	0·9290	45·22	52·89	41·97
0·9889	6·48	8·07	6·40	0·9265	46·39	54·12	42·95
0·9884	6·81	8·48	6·73	0·9245	47·32	55 08	43·71
0·9877	7·29	9·06	7·19	0·9225	48·24	56·03	44·47
0·9872	7·63	9·48	7·53	0·9205	49·16	56·97	45·21
0·9866	8·05	10·00	7·94	0·9180	50·29	58·13	46·13
0·9860	8·48	10·52	8·35	0·9160	51·20	59·05	46·86
0·9854	8·91	11·05	8·77	0·9140	52·09	59·95	47·57
0·9849	9·28	11·50	9·13	0·9115	53·21	61·06	48·46
0·9843	9·72	12·05	9·56	0·9095	54·10	61·95	49·16
0·9838	10·10	12·50	9·92	0·9070	55·20	63·04	50·03
0·9832	10·55	13·06	10·36	0·9050	56·09	63·91	50·71
0·9827	10·94	13·53	10·74	0·9025	57·18	64·98	51·56
0·9822	11·33	14·01	11·12	0·9000	58·27	66·03	52·40
0·9817	11·72	14·48	11·49	0·8975	59·36	67·08	53·23
0·9811	12·20	15·07	11·96	0·8955	60·23	67·91	53·89
0·9807	12·52	15·46	12·27	0·8930	61·31	68·94	54·71
0·9801	13·00	16·04	12·73	0·8905	62·39	69·95	55·51
0·9796	13·41	16·54	13·13	0·8880	63·47	70·96	56·31
0·9791	13·82	17·04	13·52	0·8855	64·54	71·96	57·10
0·9786	14·23	17·54	13·92	0·8830	65·61	72·94	57·88
0·9781	14·65	18·04	14·31	0·8805	66·67	73·92	58·66
0·9776	15·06	18·54	14·71	0·8775	67·95	75·07	59·57
0·9771	15·48	19·04	15·11	0·8750	69·01	76·02	60·33
0·9766	15·90	19·55	15·51	0·8725	70·06	76·97	61·08
0·9761	16·32	20·05	15·91	0·8695	71·33	78·08	61·97
0·9756	16·73	20·55	16·31	0·8670	72·37	79·00	62·69
0·9751	17·15	21·06	16·71	0·8640	73·63	80 09	63·56
0·9747	17·49	21·46	17·03	0·8615	74·67	80·99	64·27
0·9741	17·98	22·06	17·50	0·8585	75·91	82·05	65·11
0·9736	18·40	22·55	17·90	0·8555	77·15	83·10	65·94
0·9731	18·81	23·05	18·29	0·8530	78·17	83·96	66·63
0·9726	19·22	23·54	18·68	0·8500	79·40	84·97	67·43
0·9721	19·63	24·02	19·07	0·8470	80·62	85·97	68·23
0·9716	20·04	24·51	19·45	0·8440	81·83	86·95	69·00
0·9710	20·52	25·08	19·91	0·8405	83·23	88·08	69·90
0·9705	20·92	25·56	20·28	0·8375	84·42	89 02	70·65
0·9695	21·71	26·50	21·03	0·8340	85·80	90·09	71·50
0·9685	22·49	27·42	21·76	0·8310	86·97	90·99	72·21
0·9675	23·25	28·32	22·47	0·8275	88·31	92·01	73·02
0·9665	24·00	29·20	23·17	0·8240	89·64	93·00	73·80
0·9655	24·73	30·06	23·86	0·8200	91·13	94·09	74·66
0·9645	25·45	30·91	24·53	0·8165	92·41	95·00	75·39
0·9630	26·51	32·14	25·50	0·8125	93·85	96·00	76·19
0·9620	27·19	32·93	26·13	0·8080	95·43	97·08	77·04
0·9605	28·19	34·10	27·06	0·8040	96·79	97·99	77·76
0·9590	29·17	35·22	27·95	0·7990	98·46	99·05	78·61
0·9580	29·81	35·95	28·53	0·7925	100·00	100·00	79·36
0·9565	30·74	37·02	29·38				

There are also Tables by Hehner, Haas, Tralles-Brix, Gay-Lussac, &c., which differ little (at most 0·1 to 0·2 per cent.) from that of Windisch.

For any specific gravity not given in the Table the corresponding alcoholic degree can be obtained easily and with sufficient accuracy by proportional interpolat

liquid takes place through the tubes and reservoir. When the mercury thread of the thermometer remains stationary owing to the water boiling and the steam hence having a constant temperature, the scale is adjusted by the screw, E, so that the zero-point corresponds with the end of the mercury column. The reservoir is then emptied, rinsed out with the wine, &c. (containing less than 15 per cent. of alcohol), and then filled with the wine to the upper mark, so that the thermometer bulb dips into the liquid when the cover is screwed on. The condenser is filled with cold water, the burner lighted, and the heating continued until the thermometer again shows a constant reading; the corresponding scale-reading then gives directly the percentage of alcohol by volume. In the case of sweet wines or beers it is advantageous to dilute with an equal volume of water, the result given by the instrument then being doubled.

An ingenious and simple *capillarimeter*, recently devised by Bosia and constructed by the Italian Œnological Agency, Milan, gives the alcoholic strength of wines or spirits with sufficient accuracy in three or four minutes.

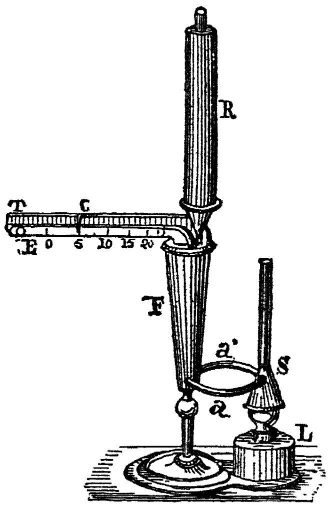


FIG. 148.

The Table given in the footnote [1] indicates the volume of water to be added to 100 c.c. of alcohol of known strength in order to bring it to a definite lower concentration. This Table is calculated from the formula:

$$x = 100\left(\frac{S'x.v}{V'} - S\right)$$

where v is the strength of the more concentrated alcohol, S its specific gravity, S' and V' the specific gravity and alcoholic strength required, and x the quantity of water to be added to 100 c.c.

STATISTICS, FISCAL REGULATIONS, DENATURED ALCOHOL. The *annual production* of alcohol is now about 21,000,000 hectols.,[2] and of this 23 per cent. is made in Germany (the taxation amounting to £7,600,000 in 1907 and £8,000,000 in 1909; in 1911 the consumption of alcohol in Germany fell to 3,650,000 hectols.), 20 per cent. in European Russia, 16 per cent. in Austria-Hungary, 14 per cent. in France, 15 per cent. in the United States, 10 per cent. in England, and 1·4 per cent. in Italy. In 1908 Turkey imported about 175,000 hectols. of alcohol (one-half from Russia).

[1]

Concentration desired	Given Alcohol at 95 % by vol.	90 % by vol.	85 % by vol.	80 % by vol.	75 % by vol.	70 % by vol.	65 % by vol.	60 % by vol.	55 % by vol.	50 % by vol.
90%	6 4									
85	13 3	6·56								
80	20·9	13·79	6 83							
75	29·5	21·89	14·48	7·20						
70	39·1	31·10	23 14	15·35	7·64					
65	50·2	41 53	33·03	24·66	16 37	8·15				
60	63 0	53·65	44 48	35·44	26·47	17·58	8·76			
55	78·0	67·87	57 90	48·07	38·32	28·63	19·02	9·47		
50	95·9	84 71	73 90	73·04	52·43	41 73	31·25	20·47	10·35	
45	117·5	105 34	93 30	81·38	69·54	57·78	48 09	34·46	22·90	11·41
40	144 4	130·80	117 34	104·01	90·76	77·58	64·48	51·43	38 46	25·55
35	178·7	163·28	148 01	132·88	107·82	102 84	87·93	70·08	58 31	43·58
30	224·4	206·22	188·57	171·05	153·53	136 34	118 94	101·71	84 54	67·45
25	287·0	266 12	245 15	224·30	203 61	182·83	162·21	141·65	121·16	100·73
20	381·8	355·80	329 84	304·01	278 26	252 58	226·98	201·43	175·96	150 55
15	539·5	505·27	471 00	436·85	402 81	368 83	334·91	301·07	267·29	233·64
10	859·0	804·50	753 65	702·89	652 21	601 60	551 06	500·50	460·19	399 85

c.c. of water to be added to 100 c.c. of the more concentrated alcohol.

For example, if an alcohol of 90 per cent. by volume is to be diluted to 50 per cent. by volume, to 100 c.c. of the former must be added 84·71 c.c. of water.

[2] See Table on next page.

For every 100 litres of alcohol consumed as beverages the following amounts are used for industrial purposes: 54 litres in Germany, 19 in Austria, 18 in France, and 14 in England.

These figures indicate the countries where *alcoholism* is causing the greatest amount of harm.[1]

PRODUCTION OF ALCOHOL IN THOUSANDS OF HECTOLITRES

	1902–3	1904–5	1905–6	1907–8	1908–9	Observations
Germany . .	3383	3791	4020		4500	
Austria-Hungary .	2318	2480	2700		2650	
Russia . . .	3855	4196	4500		2700	
United States . .	2900	2900	2900			
France . . .	1800	2500	2700	2538		
England . .	1297	1300	1284	1400		
Holland . . .	354	367	351			
Belgium . .	328	329	389			
Sweden . . .	186	195			220	(Imports in 1909 : 12,000 hectolitres)
Italy . . .	173	300	293	463		
Denmark . .	169	155	154			

In Germany the exportation varies considerably: 313,400 hectolitres in 1902, 14,000 in 1904, 194,000 in 1906, and 9700 in 1908.

[1] **Alcoholism.** The abuse of alcoholic beverages is leading to the ruin and decadence of certain nations, since it is largely the cause of depopulation and produces actual decay of the human organism Alcoholism produces a diminution in stature, as is shown by the increased numbers of those unfit for military service; it quickly leads to crime and folly, and renders the organism easily attackable by all kinds of disease, its effects being felt to the third generation.

Alcohol acts as a poison which first excites and exalts, then intoxicates and depresses the psychic faculty more or less permanently. The abuse of wine and spirits is the real cause of much intestinal catarrh and of certain visceral lesions, and sometimes leads to chronic nephritis, heart-injury, enlargement and inflammation of the liver, hepatic cirrhosis, cerebral apoplexy, progressive paralysis, and often to madness.

Among the industrial classes it is thought that alcohol warms, prevents cold, and gives greater strength during work, but this is a great error based on appearances. Almost as soon as it is swallowed, the alcohol of wine and spirits is absorbed by the blood by means of the capillaries and brought into contact with all parts of the organism, the nervous centres are then more or less paralysed, and the numerous capillaries under the skin dilate, since an increased amount of blood rushes to the skin itself. The drinker has, indeed, a red face; but the sensation of great heat is only superficial; if the surroundings are cold, the heat of the body is more easily dispersed This explains why drunken men, sleeping on the roads in the winter, readily die of cold. Nansen, the famous Polar explorer, withstood temperatures 52° below zero without using alcoholic liquors.

The International Congress on Industrial Diseases, held at Milan in 1906, declared that the use of alcohol "is unnecessary for the nourishment of the workman, and becomes harmful where the work is heavy or long. As regards useful effects in the food rations of the worker, alcohol may be advantageously replaced by sugar, coffee, and tea." Alcohol may diminish the using-up of fat in the organism and hence the consumption of proteins, but as a food it is very costly and of little effect.

During the last few years *alcohol-free wines* have been prepared by crushing grapes from the best vineyards and subjecting the must to filtration and pasteurisation (heating to 60°) so as to render it clear and prevent fermentation; the wine is then stored in hermetically sealed, sterilised bottles. These wines retain the taste and fragrance of the grape and have considerable nutritive value since the sugar of the grape remains unchanged (15 to 20 per cent.).

Alcohol also has a harmful effect on the reproduction of man, this explaining the *slowness* or absence of the increase in population of nations consuming much alcohol; as in France, where £6,000,000 was spent in 1898 on so-called aperitives (absinthe, bitters, &c) alone. In England £60,000,000 is spent annually on spirits, and in Switzerland even £6,000,000. Drink causes the direct or indirect death of about 45,000 people annually in France, 40,000 in Germany, 50,000 in England, 20,000 in Belgium, and 100,000 in Russia. In Italy, L. Ferriani stated that 627 cases of death in 1904 were evidently due to acute alcoholism. Dr. Marambat affirms that in France 72 per cent. of the criminals and 70 per cent. of the individuals (121,688) appearing annually before the courts make excessive use of alcoholic liquors. In Germany, A. Baer found that 41 7 per cent. (13,706) of the prisoners (32,837) were addicted to drink; in Switzerland, it is 41 per cent.; and in England, 33 per cent. of those sentenced at the Assizes. In Holland, four-fifths of the crime is attributed to alcohol, and in Sweden three-fourths. Similar figures to the above have been given for Italy. In various countries it has been found that 25 per cent. of the lunatics are excessive alcohol drinkers In the Salpêtrière Hospital of Paris, 60 out of 83 babies afflicted with epilepsy had alcoholic parents. In Germany, 30,000 persons are attacked every year by alcoholic delirium and other cerebral disturbances due to abuse of alcohol.

Alcoholism in Germany was a national calamity as early as the fifteenth and sixteenth centuries, when to the enormous consumption of beer was added that of brandy and, after 1550, of cereal and potato spirit. After the eighteenth century, when the production of cereal and potato spirit became a great industry, their consumption as beverages increased enormously. In 1905 the annual expenditure for alcoholic drinks amounted to 47*s.* per head, or £8 for every person over fifteen years old, making a total of £120,000,000 for the whole of Germany, or about £80,000,000 for the working classes corresponding with 12 per cent. of their wages. Every year there are 200,000 cases of inebriety, and 75 per cent of the crimes against the person are the result of drunkenness. The question of alcoholism is closely connected with the social problem, as it is especially among the working classes and the ignorant and ill-nourished that the victims are found.

Abstainers are less liable to illness and usually live longer, as is shown by the following statistics. The Tables of the Sceptre Life Association for eleven years (1884–1894) show that the mortality in the temperance section

In 1874 the average consumption of alcohol per inhabitant in Italy amounted to 6·5 litres, and in 1898 to 10·23 litres, to which must be added about 100 litres of wine.[1]

In Italy the production was 80,000 hectolitres in 1878; 165,000 in 1888; 187,000 in 1898–9; 306,700 in 1904–5, 90,000 being from cereals, 72,600 from molasses, 59,000 from wine, 83,000 from vinasse, and 1725 from fruit. In 1907–8 Italy produced 463,000 hectolitres and exported 64,000 in 1908 (half in bottles); 134,000 in 1909, 40,000 being in bottles and 7000 sweetened or rendered aromatic for beverages, and 95,000 in 1910.

In 1903 there were 3275 distilleries in Italy employing 8670 workmen. In 1904–5 spirit factories consumed 234,000 quintals of maize, 6000 of durra, and 17,000 of barley, rye, millet, and rice; also 280,000 quintals of molasses and sugar and 53,000 of other materials. To these must be added 575,000 hectolitres of wine, 2,600,000 quintals of vinasse, and 13,700 of fruit.

In Germany 80 per cent. of the alcohol comes from potatoes (the cultivation of which occupies 3,300,000 hectares out of a total area of 26,000,000 hectares capable of cultivation); in Austria 60 per cent., in Russia 50 per cent., and in France 20 per cent.; the rest is obtained from cereals and saccharine products.

The origin of the alcohol produced in France is as follows, the numbers representing hectolitres:

	From starchy matters	From molasses	From beetroot	From wine	From cider	Total
1877 . .	163,204	642,709	272,883	157,570	9,468	1,308,881
1885 . .	567,768	728,523	465,451	23,240	20,908	1,864,514
1897 . .	484,637	734,819	798,484	83,719	26,579	2,208,140
1901 . .	269,074	1,006,933	578,628	330,966	115,220	2,437,964
1904 . .	380,710	626,722	992,149	88,509	—	2,181,362
1908 . .	362,500	448,000	1,260,000	468,000	—	about 2,600,000

In Italy the tax for manufacturing alcohol was 21*s.* per hectolitre at 100 per cent. in 1871, £4 in 1883, £6 in 1885, and £7 4*s.* in 1887; to this the sale-tax of £2 8*s.* was added

(abstainers) was 57 per cent. and that in the general section (non-abstainers) 81 per cent. In times of epidemics nine out of ten non-abstainers die and only two out of ten abstainers.

The introduction of the alcoholic tendency into Africa, as a result of colonisation, wrought such havoc among the natives that the International Congresses against Alcoholism held in Brussels in 1899 and 1906 adopted various prohibitive and fiscal measures to save the black race of Africa from the terrible plague. Many remedies for alcoholism have been proposed, but singly they are almost all inefficacious, though more useful if combined.

Increase of the price of drinks and diminution of the number of shops have proved almost useless in France, Belgium, and England. In England, however, the latest increase in taxation has diminished by one-third the consumption of spirit; the amount of beer has fallen from 31·4 to 25 8 litres per head per annum, whilst the consumption of tea and wine has increased. In the United States the enormous taxes on alcohol have not diminished the consumption of liquors. Sweden has obtained good results by making a State monopoly of alcoholic drinks, by granting licence to sell only to trustworthy persons, by giving them special facilities for, and large profits on the sale of other beverages and of food, by abolishing profit on alcoholic drinks and by making the licencees responsible for cases of drunkenness on their premises. This example has been partially followed in America and England, and many temperance associations have helped by opening establishments where good food and drink are obtainable at low prices, alcohol being banned. Another effective factor against alcoholism is education and the explanation of the harm done by it: in schools, churches, barracks, the streets, workshops, books, reviews, newspapers, advertisements—indeed everywhere should an intelligent campaign be waged against alcoholic liquor which, as Gladstone said in the House of Commons, *commits more slaughter in our days than the three historic plagues: famine, pestilence, and war, since it decimates more than famine and pestilence and kills more than war, and is in all cases a disgrace often lowering man below the level of the brute.*

[1] The average annual consumption per head in litres of absolute alcohol in the form of different beverages is as follows:

	Beer	Wine	Spirits	Total
Germany	4·8	0·66	4·1	9·5
Austria-Hungary	1·7	2·1	5·1	8·9
France	1·3	17·5	3·5	22·3
England	8 3	0·2	2·3	10·8
Belgium	8·7	0·6	3·7	13·0
Denmark	2 6	—	7·0	9·6
Sweden	2·3	0·06	3·9	6·26
Russia	0·2	—	2·5	2·7
United States	3·4	0·28	2·7	6·38
Italy	0·1	12·0	2 0	14·1

In Sweden 27 litres of alcohol in the form of spirits were consumed per inhabitant in 1830,

in 1888 (so that the consumer paid about 23 pence per litre in taxation alone !); the sale-tax was abolished in 1904. A rebate of 90 per cent. of the tax is made on exported alcohol (added to marsala, vermouth, &c.). In 1903 alcohol obtained by distilling wine and vinasse and destined for industrial use was exempted of all taxation, and to alleviate the crisis in the wine industry it was proposed, but in vain, to grant a substantial bounty to the distillers of wine and vinasse. In 1911 the tax was raised to £10 16*s*. per anhydrous hectolitre at 15·56°. In 1910 the Italian exchequer received nearly a million sterling in alcohol taxes.

In Germany the manufacturing tax of ordinary non-denatured alcohol varied prior to 1909 from 64*s*. to 72*s*. per hectolitre, this being entirely repaid on exported alcohol, which in certain cases also enjoyed a bounty of 9*s*. Before 1909 the tax was based on the volume of the wort, so that all distillers tried to work with concentrated worts (up to 25° Brix). Nowadays the payment is made on the volume of anhydrous alcohol produced, and the tax varies according to the production, which is established every ten years for each factory (*contingent production*). On this *contingent* quantity the tax is 105 marks (shillings) per anhydrous hectolitre, excess production paying 125 marks. There are then supplementary taxes of 4 to 14 marks to protect the small factories, so that a hectolitre of alcohol, costing of itself 28*s*. to 32*s*., with taxes, costs £7 4*s*. to £8 8*s*. The German Government received about £8,000,000 in alcohol taxes in 1908–9 and expect in the future to raise this to £14,000,000 ; but increase in the taxation has been followed by a diminution of 25 per cent. in the consumption. Potato spirit is made in 6400 large factories, that from cereals in 730 large and 6600 small factories, that from molasses in 27 special distilleries, and that from wine, fruit, and yeast by about 60,000 small distilleries. In Germany, besides the concession of untaxed denatured alcohol to all industries, non-denatured alcohol is also allowed free of taxes to *scientific laboratories* and for medicinal uses and military explosives. The alcohol of spirituous beverages imported into Germany pays a Customs tax of about £14 16*s*. per quintal. In England the spirit duty amounted to about £30,000,000 in 1907.

In France alcohol for drinking pays a tax of £10 per hectolitre, whilst industrial spirit is untaxed (as in Germany), and is sold at about 4·5 pence per litre.

Denatured Alcohol. In several countries denatured alcohol is allowed free of tax to manufacturers, and in Italy in 1903 this spirit was taxed 12*s*. per hectolitre (100 per cent.) instead of £8 (which is subject to 25 to 40 per cent. bonus if made from vinasse or wine). Denaturation is, however, allowed only for the manufacture of ether, collodion, mercury fulminate, varnishes, photographic papers, artificial silk, and alcohol for heating or illuminating purposes. In 1905 Italy also abolished the tax of 12*s*. for denatured alcohol of whatever origin (cereals, vinasse, &c.), but there remains the cost of the denaturant, which sometimes amounts to 2*s*. 6*d*. or more per hectolitre—for about 3 per cent. of denaturant composed of methylene, acetone, pyridine, and benzene.

In order that alcohol intended for various industries may not be used for beverages (wines, liqueurs, &c.), the Government denatures it by the addition of various substances [1] —stinking, coloured, or of unpleasant taste—which cannot be separated from the alcohol

[1]

	DENATURANTS				
	Crude wood spirit	Crude pyridine	Acetone	Benzene	Crude benzine
	per cent.	per cent.	per cent.	per cent.	per cent.
France	7·5	—	2·5	—	0·5
Germany	1·5	0·5	0·5	—	—
„ (motors)	0·75	0·25	0·25	2·0	—
Austria	3·75	0·5	1·25	—	—
„ (motors)	0·5	traces	traces	2·5	—
Russia	10·0	0·5	5·0	—	—
Switzerland	5·0	0·32	2·2	—	—

In the United States methyl alcohol and pyridine are used, and, for special purposes, ether, cadmium iodide, ammonium iodide, &c.

In France denaturation costs about 10 fr. (8*s*.) per hectolitre, and the Government makes a rebate of 9 fr. In Germany it costs only 2 marks (shillings) since much less, although sufficient, denaturant is added. In Italy denaturation is possibly excessive and too expensive.

by any of the ordinary means (distillation, &c.), but which do not damage the alcohol for its industrial use. The denaturant should vary according to the use to which the spirit is to be put. There are hence in all countries a general denaturant for alcohol as fuel, for motors, &c., and special denaturants. As colouring-matter, traces of crystal violet (hexamethyl-*p*-rosaniline hydrochloride) are used in Germany. Alcohol intended for the manufacture of ether, collodion, and artificial silk is denatured by the addition of ether and sometimes of a little acetone ; in Italy, for varnishes, 2 per cent. of methylene, 2 per cent. of light acetone oils, and 20 per cent. of a 50 per cent. solution of sealing-wax are used. It has also been proposed to use part of the stinking products obtained on distilling certain bituminous shales.

In 1906–7, 41,000 hectolitres of alcohol were denatured in Italy with the general denaturant for fuel, motors, lighting, &c. (16,790 in 1903–4, about 18,500 in 1904–5, over 30,000 in 1905–6, and almost 83,000 in 1910), 1031 hectolitres for making ether (about 1100 in 1904–5 and 8120 in 1910), 38 hectolitres for collodion (63 in 1910), 130 hectolitres for the manufacture of mercury fulminate (140 in 1910), 1625 hectolitres for artificial silk in 1910, 50 hectolitres for photographic paper (1910), 995 hectolitres for lacquer according to the Dermoid patent, and 1364 hectolitres for other lacquers (1910). In France 23,000 hectolitres out of a total of 1,488,000 were denatured in 1879 ; in 1901 153,000 hectolitres with the general denaturant were used for motors and lighting, and 98,130 hectolitres with special denaturants for chemical industries ; in 1904, 290,000 hectolitres with the general denaturant and 133,500 hectolitres with special denaturants, the total production being 2,180,000 hectolitres ; in 1907, 600,000 hectolitres were denatured altogether ; and in 1908, about 626,670 hectolitres—442,758 for heating and lighting, 12,054 for varnishes, 21,300 for celluloid, 1147 for dyes, 359 for collodion, 194 for chloroform, 950 for tannin, 490 for chloral, 138,346 for ether, fulminate of mercury, and explosives, 6972 for pharmaceutical products, 587 for scientific purposes, and 1514 for other uses.

In the United States, 126,000 hectolitres were denatured in 1908 and 173,000 hectolitres in 1909 (after the law of 1907). In 1910–1911 the United States consumed 250,000 hectolitres of denatured alcohol. In Norway, in 1910, 400 hectolitres were denatured, and the consumption of spirits, which was 40,000 hetcolitres in 1874, diminished to 15,000 hectolitres in 1910.

In Germany, 1,400,000 hectolitres of denatured alcohol were sold in 1904–5 (1,582,000 hectolitres in 1908), of which 36,000 were for motors (in 1903 only 24,000 hectolitres were used for this purpose, 12,500 horse-power being developed).[1] In 1909–1910, 1,883,000 hectolitres of alcohol were denatured in Germany.

Denatured 90 per cent. alcohol now costs 46*s*. per quintal in Italy, whilst in Germany it costs only about half this, namely, 25 marks (shillings) per hectolitre (after 1909, with the new tax, 48*s*.), in Austria 26*s*., in Switzerland 24*s*. (retail), and in Belgium 25*s*.

UTILISATION OF DISTILLERY RESIDUES. All the components of the prime materials used in the production of alcohol are found (excepting the carbohydrates: starch and sugar) in the residues (grains, spent wash) left after the distillation of the alcohol.

These residues formerly formed inconvenient refuse, since they readily undergo putrefaction and, if discharged into rivers or canals, contaminate the water. In exceptional cases, when the distilleries are in large agricultural centres, the residues are used in the wet state for cattle-food, but more commonly they are evaporated and dried, these dried grains being highly valued as a concentrated fodder, rich in proteins[2] and having a restricted (1 : 3 to 1 : 5) *nutritive ratio* (ratio between nitrogenous and non-nitrogenous substances).[3] In the fresh residues two-thirds of the part which is not water is dissolved

[1] An automobile weighing 1200 kilos, on a journey of 174 kiloms. (109 miles) at 30 kiloms (19 miles) per hour, consumed 11·3 litres of alcohol; under similar conditions, 10 litres of petrol are required. For an 8 h.p. car, 350 grms. of alcohol or 500 of petrol are used per horse-power hour. For automobiles and explosion motors in general, the Paris Omnibus Company uses alcohol mixed with 50 per cent. of benzene, this giving a better thermal efficiency (34 per cent.). A domestic 25-candle lamp with an Auer mantle uses about 2 grms. of alcohol per candle-hour. The use of *alcoholene*, a mixture of alcohol and ether, has now been proposed, and from a technical standpoint presents advantages over alcohol and other mixtures.

[2] The average percentage compositions of the principal residues will be found in the Table on page 154.

[3] For *fodder*, the *nutritive values* of the proteins, fats, and non-nitrogenous digestible substances are in the proportions 3 : 2 : 1, so that the *commercial value of a fodder*, expressed in *nutritive units*, is given by : nitrogenous substances × 3 + fatty substances × 2 + non-nitrogenous substances, given by the percentage composition of the *digestible* components.

and the remaining third suspended in the water. Potatoes give about 10 per cent. of dried residue, malt about 40 per cent., and maize 45 to 50 per cent.

It will hence be understood how distilleries have greatly increased the raising of cattle and consequently production of stable manure, thus contributing to the fertilisation of formerly unfertile lands.

The economics of the drying of these residues has always constituted a difficult problem owing to the presence of more than 90 per cent. of water in which part of the nutritive products is dissolved and to the fact that the dried residues sell at 8*s*. to 11*s*. per quintal. In many cases the liquid portion is abandoned and the solid part separated by filter-presses or centrifuges ; but if the liquid part cannot be got rid of, even after addition of lime, ferrous sulphate, &c., it is best to evaporate it by means of the hot fumes from the flues, the operation being hastened with disc-stirrers of large surface and with fans. The evaporation is sometimes carried out in a vacuum apparatus (*see* Sugar) furnished with stirrers, by which means a marked economy in fuel is effected (*see also* vol. i, pp. 442–444).

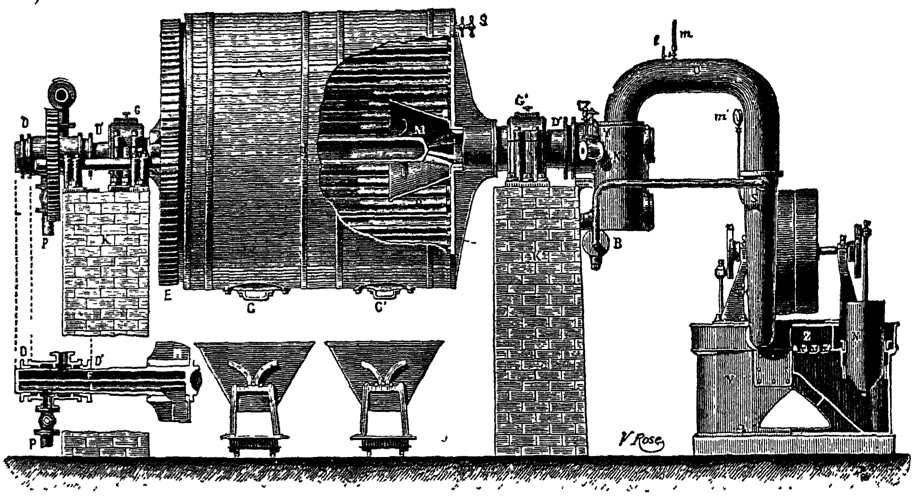


FIG. 149.

Of the various drying systems (Hatschek, Meeus, Porion and Méhay, Venuleth and Ellenberg, Theisen, Büttner and Meyer, &c.), we shall only deal with that of Donard and Boulet, which has been applied with advantage in France and recently also in Italy.

The solid residue from the filters or centrifuges (perhaps mixed with the evaporated residue of the liquid portion), still containing more than 50 per cent. of water, is carried by mechanical transporters into the vacuum drying apparatus (Fig. 149), consisting of a horizontal cast-iron cylinder rotatable about a hollow axis through which the steam enters or issues ; its length and diameter are 2·5 metres. Inside are a number of tubes (heating area about 60 sq. metres) into which steam is passed from *D*, the condensed water being discharged without coming into contact with the mass to be dried. At the

TABLE OF AVERAGE PERCENTAGE COMPOSITIONS OF THE PRINCIPAL RESIDUES

	Beetroot		Potato		Rye		Maize		Durra		Barley	
	liquid	dried	liquid	dried	liquid	dried	liquid	dried	liquid	dried	liquid	dried
Water	91·0	10–12	94·0	8–10	91·0	10–12	90·6	10–12	90·3	10–12	75·0	14·0
Proteins	0·9	6–7	1·3	18–24	1·9	22–28	2·0	24–26	2·0	24–26	4·0	20·0
Non-nitrogenous matter	7·2	60–65	2·6	45–55	5·2	48–52	4·9	35–40	5·1	30–34	10·0	46·0
Fatty matter		1·3–1·6	0·2	3–4	0·3	5–6	1·0	12–16	0·7	12–14	1·7	7·0
Cellulose	0·9	13–15	0·9	9–11	1·0	5–7	1·0	10–12	1·1	14–16	5·0	16·0
Ash		10–12	0·5	1–2	0·6	4–6	0·5	5–6	0·8	7–8	1·3	5·0

other end, by means of the perforated axis, *G'*, the interior of the cylinder communicates with a double-action exhaust pump to carry away the vapour from the grains which are heated in a vacuum of 700 mm., while the cylinder slowly rotates (three turns per minute). The charge consists of 25 to 30 quintals of solid grains, which are dried (to 15 per cent. moisture, it then keeping well) in less than four hours, the coal consumption being about 150 kilos. By thus drying at a relatively low temperature (in a vacuum) and out of contact with air, the oil of the grains does not become rancid.

Since maize-grains contain as much as 15 to 18 per cent. of fat, it is sometimes convenient to extract them in one of the forms of apparatus described in the section on Fats.

Special interest attaches to the residues from **Molasses** and **Beet**, since these contain special nitrogenous compounds (amino-acids) and a large proportion of potassium salts utilisable for fertilisers or for chemical products. The evaporation of the liquid part of these residues may be carried to a certain stage in the ordinary vacuum plant, the mass being subsequently completely evaporated and the residue calcined in suitable furnaces (Porion model in France and Belgium) which are similar to the reverberatory furnaces or muffles used in the preparation of sodium sulphate (*see* vol. i, p. 161). Care must be taken not to fuse the mass, which, when discharged, should still be carbonaceous and, indeed, sufficiently so to cause it to burn when placed in heaps outside the furnaces; the greyish mass thus obtained—known in France as *salin*—contains: water, 0·3 to 6 per cent.; KCl, 6 to 10 per cent.; K_2SO_4, 10 to 14 per cent.; potassium phosphate, 0 5 to 1 per cent.; K_2CO_3, 53 to 58 per cent.; Na_2CO_3, 6 to 9 per cent.; soluble substances, 9 to 14 per cent. By this treatment, however, all the nitrogen compounds are lost; but in some cases these are used for the extraction of methyl chloride (*see* p. 96). The process for extracting pure potassium carbonate, ammonia, and sodium cyanide is referred to in vol. i, p. 435.

During recent years the utilisation of these nitrogenous substances has assumed great importance: according to the Effront patents (1907), the amino-acids are utilised by enzymic processes[1] for the preparation of organic acids and ammonium sulphate (with each hectolitre of alcohol produced correspond 25 kilos of ammonium sulphate and 35 grms. of organic acids, principally acetic, propionic, and butyric). Since 1902, the Dessau Sugar Refinery, and since 1904 the Ammonia Company of Hildesheim, have utilised the nitrogen compounds as potassium cyanide and ammonium sulphate. In 1907 the Ammonia Company utilised 60 per cent. of the nitrogen of the residues, producing potassium cyanide to the value of £80,000 and ammonium sulphate to the value of £20,000.

ALCOHOLIC BEVERAGES

WINE. Only the liquid obtained by the spontaneous alcoholic fermentation of the must of fresh grapes, without any addition, should be called wine. The fermentation is spontaneous owing to the presence on the grapes of *Saccharomyces cerevisiæ*.

Grape must has the sp. gr. 1·08 to 1·10 and contains 70 to 86 per cent. of water, 16 to 36 per cent. of sugar (glucose and levulose, which reduce Fehling's solution); 1 to 3 per cent. of cream of tartar, tartaric, malic, and tannic acids; 0·4 to 1 per cent. of colouring, aromatic, extractive, gummy, and protein substances, and mineral salts. If the musts have to be transported over long distances, either they are concentrated in a vacuum or by freezing, or the fermentation is interrupted for a time by filtering them. One quintal of grapes gives 60 to 70 litres of must and 30 to 35 kilos of residue (marc).

By fermentation in open vats the sugar is transformed, more or less completely, in 7 or 8 days into alcohol, large quantities of carbon dioxide being developed and a little glycerol, succinic acid, &c., always being formed. With more than 25 per cent. of sugar, *sweet wines* are obtained, and with less, *dry wines*. Fermentation cannot yield more than 15 to 16 per cent. of alcohol, as with more than this proportion the yeast dies. After the principal fermentation, when the wine, without the marc, is placed in casks of chestnut or oak, a slow fermentation goes on, this ceasing in the winter; with increase in the alcohol-content and lowering of the temperature, the yeast and part of the tartar

[1] Ehrlich was the first to show that the fermentation of amino-acids is produced by *amidases*. Effront (1908) found that amidases occur especially in top beer-yeasts and in aerobic yeasts which, in seventy-two hours at 40° are able to transform, *e.g.* all the nitrogen of an alkaline asparagine (*see this*) solution, and almost all the nitrogen of the yeast itself into ammoniacal nitrogen, organic acids being formed at the same time.

(slightly soluble in alcoholic liquids) are deposited. In the spring, the clear wine is decanted into clean (sulphured?) casks, which are kept full. It can now be placed on the market, or it can be further matured by clarifying it in the cask (by shaking with albumin and a little tannin and allowing to stand) and by decanting and filtering it several times during the course of a year or more before placing in well-cleaned bottles; the latter are corked by machinery with paraffined corks. As time goes on, the wine acquires a pleasing aroma, this process being hastened sometimes by *pasteurisation*, which consists in passing the wine rapidly through coils heated to about 60°; this process also arrests certain incipient diseases, which would otherwise end by spoiling the wine (acidity, &c.). Sparkling wines are obtained by saturating the cold wine with carbon dioxide during bottling or by bottling sweet wines, the fermentation of which continues slowly in the corked bottle; in the latter case, however, a deposit forms at the bottom of the bottle.

In order to obtain wines of constant type on a large scale, co-operative wineries have been recently instituted in France, these collecting the grapes or must from a whole district, mixing it and preventing it from fermenting by saturating it in the cold with sulphur dioxide (70 grms. liquid SO_2 per hectolitre); in this way, not only the yeasts, but also the moulds, bacteria, and unpleasant odours are destroyed and the must can then be kept for months in closed vessels. When part of the must is to be converted into wine, it is heated at 50° to 60° in a vacuum by allowing it to pass down a kind of rectifying column (Barbet, Ger. Pat. 195,235, 1906), the sulphur dioxide thus removed being recovered; selected yeast or other wine rich in yeast is then added, the resulting wines being of uniform and improved character, although somewhat rich in sulphates. These desulphurated musts might well be used as *non-alcoholic* wines. There are also special yeasts capable of destroying SO_2 in the musts and of starting fermentation. In Italy much has been said in favour of co-operation in 1909 and 1910, but no trial has been made on a large scale.

The proportions of the most important components of wine vary between wide limits, owing to variation of the vines, soil, climate, system of wine-making, and season (certain wines contain manganese, sometimes as much as 27 mgrms. per litre).

It is hence difficult to ascertain if there has been an artificial addition of constituents similar to those naturally present in the wine, so that considerable dilution with water and addition of alcohol, glycerol, tartar, sugar, &c., are not easy to detect if they do not exceed such limits. *Natural wines* may contain 8 to 16 per cent. of alcohol, 1·6 to 4 per cent. (for dry wines, and as much as 20 per cent. or more for sweet wines) of dry extract (obtained by evaporating a definite volume to dryness on a water-bath and drying in an oven at 100°), 0·5 to 1·5 per cent. of various acids and tartar (expressed as tartaric acid) and 0·15 to 0·45 per cent. of mineral substances (*ash*, obtained by calcining the dry extract); the glycerol varies from one-seventh to one-fourteenth part of the alcohol. Naturally these variations are much smaller for wines of a certain quality and year and obtained from one and the same district, for which the results of numerous analyses have been collected.

In Italy the following *minimum* legal limits have been recently (Ministerial Circular, 1907) established as those which must be reached for a wine to be called natural (except in cases where *genuine* wines of the same origin and year are shown to give lower limits): alcohol, 8 per cent. by volume in white wines, 9 per cent. in red; dry extract without sugar, 1·6 (white), 2·1 (red); total acidity expressed as tartaric acid, 0·5 (white), 0·6 (red); ash, 0·15 (white), 0·2 (red); alkalinity of the ash in c.c. of normal alkali per litre, 11 (white), 16 (red); the glycerol should be from one-seventh to one-fourteenth by weight of the alcohol, and the relation between ash and extract (for dry wines or for sweet wines after deducting the sugar) should be about 1 : 10; *plastering*,[1] expressed as sulphuric acid, should not exceed 0·02 per cent.

In France, and now also in Italy, watering of a wine is detected by adding the percentage of alcohol by volume to the total acidity per litre expressed as sulphuric acid; this should give 13·5 for red and 12·5 for white wines (in Milan, 12·5 is allowed for red and 11·5 for white wine). Wines weak in alcohol or tartar do not keep well in the warm

[1] In order to prevent certain diseases to which southern wines low in acidity are liable, recourse is had to *plastering*, *i.e.* the addition of sulphites or bisulphites, which increase the quantities of sulphuric acid and sulphates. Thus some wines remain clear in the bottle, but become turbid and dark on exposure to the air; this disease, termed *casse*, is prevented by addition of potassium bisulphite, which also arrests secondary fermentation. To make certain weak wines keep better in summer in tapped casks, calcium sulphite is added, this giving a slow evolution of sulphur dioxide.

weather. A weak wine can be improved by either mixing with stronger wines or concentrating by freezing, water then separating in the form of ice (this method, in use even in the Middle Ages, has recently been patented in Italy !)

New wine has sometimes the smell and taste of rotten eggs, *i.e.* of hydrogen sulphide ; this can be remedied by decanting it into casks in which sulphur has been burnt: $2H_2S + SO_2 = 2H_2O + 3S$.[1]

From the vinasse remaining after the wine is drawn off a little rather rougher wine can still be obtained by subjecting it to considerable pressure, and from the pressed vinasse alcohol (*see above*) and tartar (*see later*) can be extracted.

The testing or analysis of wine is usually limited to determining the alcohol (by the method described on p. 146), dry extract, ash (*see above*), glycerol, plastering, and total acidity, and to testing for the addition of colouring-matter and other adulterations.[2]

Statistics. The countries which produce the most wine are France, Italy, and Spain. For Italy the statistics are very contradictory, and even the official ones are erroneous ; for instance, the production for 1909, which was given officially as 40,000,000 hectols. was officially corrected in 1910 to 60,000,000 hectols.

[1] To desulphur musts and wines, use is sometimes made of a small quantity of *urotropine* (*hexamethylenetetramine*) ; such addition can be detected, according to Fonzes-Diacon and Bonis (1910) by distilling 25 c.c. of the wine with 3 drops of sulphuric acid, acidifying the first 5 c.c. of distillate with 1 c.c. of sulphuric acid, and observing if it colours a solution of fuchsine decolorised with sulphur dioxide. The residue from the distillation is rendered alkaline with magnesium hydroxide and distilled, the vapours distilling over being condensed in a known volume of N/10 sulphuric acid, which is titrated back to ascertain how much ammonia distils over from the urotropine.

[2] The Total Acidity is estimated by titrating 10 c.c. of the wine, diluted with water, with N/10 sodium hydroxide solution, using blue litmus paper as indicator; multiplication of the number of c.c. of NaOH by 0·75 gives the total acidity in 100 c c, *expressed as tartaric acid.* A *volatile acidity* (acid that distils in a current of steam) exceeding 0·1 per cent., expressed as acetic acid, indicates a sour wine.

The Glycerol is determined by evaporating 100 c.c. of wine to about 10 c.c. on the water-bath, then adding sand and milk of lime until it is strongly alkaline and evaporating to dryness; the residue is taken up in 50 c.c. of 95 per cent. alcohol, the solution boiled and filtered, and the residue washed with 150 c.c. of hot alcohol; the filtrate is then evaporated on the water-bath to a syrup, which is well mixed with 10 c.c. of absolute alcohol and 15 c.c. of ether, allowed to deposit, filtered into a tared dish, the residue on the filter being washed with a mixture of equal volumes of alcohol and ether. Evaporation of the solvent leaves the glycerol, which is dried in a steam-oven and weighed.

Plastering is allowed by law up to a maximum quantity of total sulphuric acid (of sulphates) corresponding with 2 grms. of normal potassium sulphate per litre. Hence, on adding to 50 c.c. of the wine, 50 c.c. of a solution of $BaCl_2$ (2·8 grms. of the crystallised salt and 50 c.c. of HCl to a litre), boiling, allowing to stand, and filtering, the filtrate should give no further precipitate with barium chloride solution, that already added being exactly sufficient to precipitate the maximum allowable amount of potassium sulphate. Excessive *sulphuration* of wines is sometimes masked by the addition of *urotropine* (*see above*), which decomposes into ammonia and formaldehyde, the latter fixing the sulphurous anhydride; this can, however, be detected by Schiff's reaction (*see* Aldehydes).

Artificial Coloration. 100 c.c. of the wine are evaporated to about one-third the volume, 3 to 4 c.c. of 10 per cent. HCl and 0·5 grm. of well defatted white wool being then added and the liquid boiled for five minutes; the solution is then poured off, and the wool, after being thoroughly rinsed in running water, is repeatedly boiled with fresh quantities of water acidified with HCl until the latter no longer becomes coloured; the wool is again well washed with water and boiled for ten minutes with 50 c.c. of water and 15 to 20 drops of concentrated ammonia solution, the wool being then removed and the boiling continued to expel the ammonia; the liquid is then slightly acidified with HCl and boiled for five minutes with fresh wool. If the latter, after washing, remains distinctly red, the presence of artificial coal-tar colours in the wine may be certified; but if the colour of the wool is faint or indefinite, the colour is removed with water and ammonia, and the solution acidified and boiled with fresh wool; even a faint red coloration of this confirms the presence of coal-tar dye.

L. Bernardini (1910) finds that if the lower end of a strip of filter-paper is dipped into wine coloured with vegetable or animal substances, these rise to a greater height than the œnocyanin, which is more tenaciously fixed; hence, after the paper has been dried, different parts can be tested for artificial colouring-matters by the characteristic general reactions (*see* Table of Colouring-Matters in Part III).

It has been observed recently that the natural colours are slowly decolorised (in 48 hours) by hydrogen peroxide, whilst the artificial ones are not.

Salicylic Acid and Saccharin are detected as in beer (*see later*).

Added *water* is difficult to recognise if it does not bring the constituents of the wine below the legal limits (*see above*), and sometimes as much as 40 per cent. of water can be added to strong wines without reaching these limits. However, since natural wines never contain nitrates, which are present in almost all waters, the following test may be made: 100 c.c. of the wine are treated with 6 c.c. of lead acetate solution and filtered. To the filtrate are added 4 c.c. of concentrated magnesium sulphate solution and a little pure animal charcoal, the liquid being shaken, allowed to stand a short time, and then filtered. To a few drops of the decolorised liquid are added a few crystals of diphenylamine and 1 to 2 c.c. of concentrated sulphuric acid. If a blue coloration is formed, the presence of nitrates is demonstrated—the reagents being assumed to be pure. If the wine is watered with distilled or condensed water, or pure rain water, the reaction for nitrates is not given.

The addition of Glucose to wine or liqueurs is detected by adding to the wine a little pure yeast (pressed yeast) so as to ferment completely any grape-sugar still present as well as the added glucose. Commercial glucose, prepared from starch, always contains a small quantity of unfermentable, dextro-rotatory substances, so that if the wine, after fermentation is complete (when no more CO_2 is evolved) and after decolorisation with animal charcoal or with a little lead acetate, still exhibits a dextro-rotation greater than 0·5° in a 20 cm. tube, the presence of glucose is proved.

The following figures represent hectolitres (1 hectolitre = 22 gallons):

	France	Italy	
	Production	Production	Exportation
1875	83,000,000	28,000,000	363,000
1879	25,000,000 (phylloxera)	34,000,000	1,075,000
1884	34,781,000	21,000,000	2,380,000
1887	24,333,000	34,000,000	3,603,000 (2,800,000 to France)
1889	23,000,000	22,000,000	1,440,000 (commercial treaty with France broken in 1887)
1893	59,000,000	32,000,000	2,362,000 (750,000 to Austria-Hungary; 300,000 to Switzerland,[1] and 426,000 to America)
1897	32,000,000	28,000,000	2,400,000
1901	58,000,000	44,000,000	1,334,000
1902	—	35,000,000	2,164,000 (976,300 to Austria-Hungary).
1903	39,000,000	—	—
1904	—	42,000,000	1,200,000 (Austro-Hungarian market lost by new commercial treaty)
1905	57,000,000	28,000,000	980,000 (worth £1,400,000)
1906	62,000,000	30,000,000	710,000
1907	66,070,000	54,000,000	920,000
1908	66,500,000	52,000,000	1,200,000
1909	66,000,000	60,000,000	1,450,000 (France has a vine area of 1,625,630 and Italy of 3,500,000 hectares)
1910	—	42,000,000	2,000,000

In the Italian exportation is included that of marsala, vermouth, and bottled wine, this amounting in 1885 to 1,200,000 bottles and flasks (including vermouth and marsala), in 1894 to 3,000,000, in 1897 to 4,720,000, in 1904 to 8,120,000, and in 1905 to 9,000,000 (worth £440,000), whilst in 1891 France exported 33,000,000 bottles (worth £3,800,000) and to-day has an enormous export.

The *world's production* of wine in 1902 was 126,000,000 hectolitres: 16,000,000 in Spain, 5,200,000 in Austria, 2,000,000 in Hungary, 5,000,000 in Portugal, 3,500,000 in Algeria, 2,000,000 in Germany (formerly 3,700,000; in 1906 1,636,000 and in 1907 2,492,000 from 118,600 hectares of vineyards, in 1910 846,139 hectolitres), 2,300,000 in Russia, almost 2,000,000 in Turkey and Cyprus, nearly 1,000,000 in Greece and its islands, 2,300,000 in Bulgaria, 2,700,000 in Roumania, 500,000 in Servia, 1,100,000 in the

[1] The following is a statistical *résumé* of the wine imported into Switzerland from 1906 to 1910 (in hectolitres):

From	1906	1907	1908	1909	1910
Italy	137,843	300,208	531,776	651,726	828,559
France	273,731	581,163	363,769	386,486	216,909
Spain	123,587	219,666	415,052	352,347	422,775
Austria	53,411	78,104	69,634	91,034	110,608
Greece	9,370	10,120	12,209	42,234	64,874
Algeria-Tunis	19,520	52,501	17,342	11,118	10,714
Germany	10,009	8,870	7,619	7,650	5,504
Turkey	5,743	5,183	3,637	2,865	2,451
Other countries	50	50	62	457	—
Total hectolitres	633,566	1,255,865	1,421,290	1,546,027	1,675,427
Total value	—	—	—	£1,430,800	£2,255,840

United States, 1,500,000 in Argentine, 2,500,000 in Chili, 350,000 in Brazil, 327,000 in Australia, &c. The total production in 1909 was estimated at 160,000,000 hectolitres. The average annual consumption per head is 144 litres in France, 121 in Italy, and 116 in Spain. In Milan in 1909 duty was paid on 1,000,000 hectolitres, the Corporation receiving £420,000, and the consumption per head being 200 litres.

In 1905 Italy exported to Germany 124,000 quintals of dessert grapes, whilst France exported only 78,000 quintals. In 1892 Italy exported about 260,000 hectolitres of wine to Germany, but less amounts in subsequent years.[1]

MARSALA. This is a liqueur wine made for the first time at Trapani in 1773 by J. Woadhouse of Liverpool to compete with the world-famous Madeira. In 1812 another large establishment was started by the Englishman, Benjamin Ingham, and in 1840 Vincenzo Florio's factory which has since become the most celebrated. The prime material for the manufacture of Marsala is white Trapani wine with 13 per cent. of alcohol, to which is added (in quantity varying for different types of Marsala) the must (*cotto*) of very mature white grapes, concentrated in open boilers until two-thirds have evaporated; then is added, in varying amount, the *sifone*, obtained by filling a cask to the extent of three-fourths with clear must from a very ripe white grape, and one-fourth with pure alcohol (free from tax if for export), mixing and allowing to age so as to develop the Marsala aroma.

Mixtures of these three components in different proportions give the various brands of Marsala: the *Italian brand* is the least alcoholic (16 to 17 per cent.); the *original English brand*, the strongest (up to 24 per cent. of alcohol); while the *Margherita* and *Garibaldi brands* are of intermediate strengths and are sweeter.

In 1904 Italy exported in cask 30,540 hectolitres of Marsala, worth £92,000; in 1905, 29,765 hectolitres, worth £83,280, and 51,000 bottles, value £2040; in 1906, 26,800 hectolitres; in 1907, 27,677 hectolitres; in 1908, 24,900 hectolitres; and in 1909, 24,800 hectolitres, of the value of £97,600, together with 136,000 bottles. In 1910 the exportation was 32,500 hectolitres.

VERMOUTH. This was prepared formerly in Tuscany, but nowadays almost exclusively in Piedmont, where the industry was started in 1835 by Giuseppe Cora and A. Marendazzo.

The prime material for manufacturing vermouth is the muscat wine of Asti and of the Monferrato heights, which contains 6 to 11 per cent. of alcohol and 2 to 4 per cent. of sugar; with this is mixed 2 to 5 per cent. of a vinous infusion of aromatic drugs in which wormwood predominates and which contains also sweet flag, juniper, gentian, &c.; finally alcohol is added to bring the strength up to 15 to 18 per cent. and sugar to the density of 6° to 9° Bé. (if for exportation, 90 per cent. of the alcohol and sugar taxes are refunded). Sparkling vermouth is made by saturating it with CO_2 in the cold under pressure.

It cannot be said that in the manufacture of Marsala and vermouth all the rational methods prescribed by modern œnotechnics are followed.

The production of vermouth in Piedmont is now about 250,000 hectolitres, the exports (especially to America) being 12,400 hectolitres in cask and 31,214 hectolitres in bottle in 1902; 10,000 hectolitres (£24,000) in cask and 53,500 hectolitres (£224,000) in bottle in 1905; 8960 hectolitres in cask and 64,980 hectolitres in bottle in 1906; 8600 hectolitres in cask and 77,800 hectolitres in bottle in 1907; 7874 hectolitres in cask and 83,300 hectolitres in bottle in 1908; 10,176 hectolitres in cask (£27,680) and 100,000 hectolitres in bottle (£464,920) in 1909; 20,400 hectolitres in cask (£53,040) and 173,670 hectolitres in bottle (£760,000) in 1910.

CIDER. This is an alcoholic drink obtained by the partial fermentation of the juice of apples and pears. It is largely used in the north of France, in Germany, and in Switzerland. It is consumed almost immediately it is made. In France the production varies from 8,000,0000 to 30,000,000 hectolitres, part of which is distilled to produce alcohol (30,000 to 70,000 hectolitres of alcohol).

LIQUEURS. These contain 40 to 70 per cent. of alcohol. The finest are those obtained by collecting the first, more highly alcoholic distillate from other fermented liquors. Such are **brandy** (prepared by distilling vinasse or wine and containing 45 to 55 per cent. of alcohol), **cognac**, **kirschwasser** (obtained especially from the cherries of the Black Forest),

[1] The import duties levied by different countries on Italian wines are as follows: Germany, 29*s.* per quintal; Belgium, 18*s.* 6*d.*; Holland, 34*s.*; England, 23*s.* for wines with less than 14·84 per cent. of alcohol, and 54*s.* 6*d.* for stronger ones; Russia, 45*s.*; United States, 54*s.* 6*d.*; and British India, 33*s.* 6*d.*

rum (prepared principally in Jamaica by distilling fermented cane-sugar molasses), *maraschino* (prepared from small Zara cherries), *gin* (from juniper berries), *atole* or *chica* of South America, *arrack* of the Arabs and Indians (prepared from rice, cane-sugar, and coco-nuts), *schnapps* of the Germans (potato spirit), &c.

The other class of liqueurs comprises those obtained from aromatic substances, sugar, and more or less concentrated pure alcohol. In this way are obtained *rosoli*, *anisette*, *absinthe* (alcoholic decoction and distillation with wormwood)—much used in France and the principal cause of the terrible effects of *alcoholism* (p. 150)—*crème de menthe*, *crème de café*, &c.; *ratafia* from fruit must, spirit, and sugar; *Chartreuse* (the most celebrated was that prepared by the Carthusian monks, before their expulsion from France in 1904, from balm-mint, cinnamon, saffron, hyssop, angelica, sugar, alcohol, and other ingredients), *coca* (from Bologna), *curaçao* (first prepared from two kinds of orange in the island of Curaçao in the Antilles), *kummel* (in Russia the best kinds are obtained by distilling brandy or alcoholic liquids with Dutch cumin seeds and dissolving pure sugar in the highly alcoholic distillate). It is unnecessary to mention that all liqueurs, even the most celebrated, are more or less poorly imitated in all countries with mixtures in no way resembling the original types, but the latter always command very high prices.

Cognac is a brandy prepared especially in Charente by very carefully distilling weak wines of special vintages and refining and maturing the product in casks of Angoulême or Limousin oak, which gradually imparts to the spirit a pale yellow colour and a characteristic aroma. The finer and older brands sell at as much as £40 per hectolitre.

FERMENTED MILK. This bears the following names according to the locality and method of its preparation and the nature of the milk from which it is made: *kephir*, *koumis*, *galazin*, *leben* (Egypt), and *mazun*. The first three of these are the best known.

KEPHIR, or **Kefir**, is of very ancient origin among the Caucasian highlanders, who nowadays make enormous use of it and jealously keep the secret of its preparation. There is a legend to the effect that Allah was the first to make it, and that he recommended it as a remedy for various diseases. Kephir is simply cows' milk (fresh or skim) fermented by the addition of a special ferment in the form of granules, which the Russians call "*fungi*" and the Tartars "grain or millet of the Prophet," as they regard it as discovered by Mahomet. It was only in 1882 that Dr. Dmitrieff called the attention of the rest of Russia and of Europe to kephir and its great recuperative properties in cases of lung diseases.

Kern and, later, Freudenreich showed that the alcoholic fermentation of milk with *millet of the Prophet* is due to the simultaneous action (*symbiosis*) of the new *Saccharomyces kephiri* (similar to ordinary *Saccharomyces ellipsoideus*), a *streptococcus*, and a *bacillus*. The alcoholic fermentation of milk-sugar with evolution of CO_2 takes place rapidly and is always accompanied and followed by acid fermentation (lactic acid), which partially dissolves the casein (propeptones) and forms a very fine coagulation, almost a frothy emulsion. In practice the kephir *granules* are softened with tepid water (30° to 35°) for a couple of hours, the milk being then added and the mixture shaken every hour for eight hours; it is then sealed up in clean bottles fitted with mechanical stoppers and is shaken now and then, the temperature being maintained at 15° to 20°; in 24 hours' time the kephir is ready; it forms a slightly alcoholic and acidulated dense, frothing liquid. If the kephir is left in closed bottles for two days, the pressure increases and the mass becomes more acid and more liquid; by the third day it becomes extremely acid and contains up to about 2 per cent. of alcohol, and after this it is inadvisable to drink it.

In Italy kephir or kephir-extract is placed on the market by the Borgosatollo Dairy (Brescia) and kephir dried *in vacuo* is also prepared (Rosemberger, Ger. Pat. 198,869, 1907).

KOUMIS is similar to kephir, and of equally ancient origin, but is prepared from mares' milk. In Russia there are various sanatoria which make efficacious use of large quantities of koumis. The composition of the latter has been found to be: Water, 94 per cent.; CO_2, 0·9; ethyl alcohol, 1·7; lactic acid, 0·7; lactose, 1·3 (before fermentation 5·5); fats, 1·3; proteins, 2·3 (largely peptonised); salts, 0·3.

GALAZIN is obtained by placing skim (cows') milk, with 2 per cent. of sugar and 0·3 per cent. of beer-yeast in strong, tightly stoppered bottles, and allowing fermentation to proceed for twenty-four hours at 16°; from the second to the sixth day the proportion of alcohol rises from 0·3 to 1·5 per cent. Galazin is less nutritious than kephir or koumis.

BEER

This is another alcoholic liquor saturated with CO_2 and is obtained by fermenting aqueous decoctions of barley-malt and hops.

The ancient Egyptians were acquainted with the manufacture of beer and held it in great regard. Later it became known to the Ethiopians and the Hebrews, but the Greeks never acquired a taste for beer. The industry was taken by the Armenians from Egypt into the interior of Asia, and still later beer was manufactured in Spain and France, but it was never consumed by the Romans. In Germany beer has been made from time immemorial.

A marked improvement in the manufacture of beer dates from the time of Charles the Great, when hops were first used.

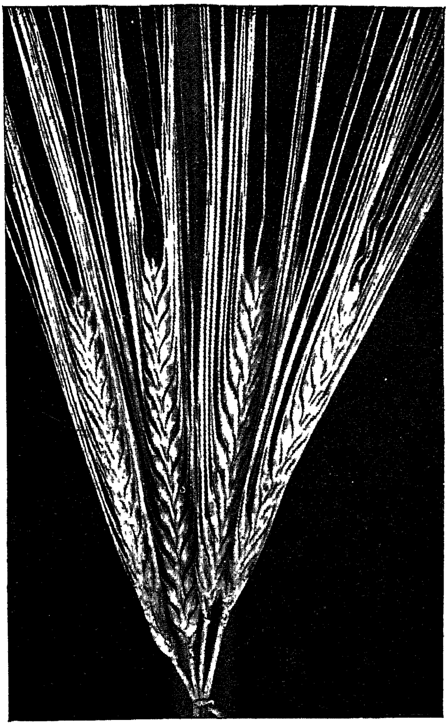


FIG. 150.

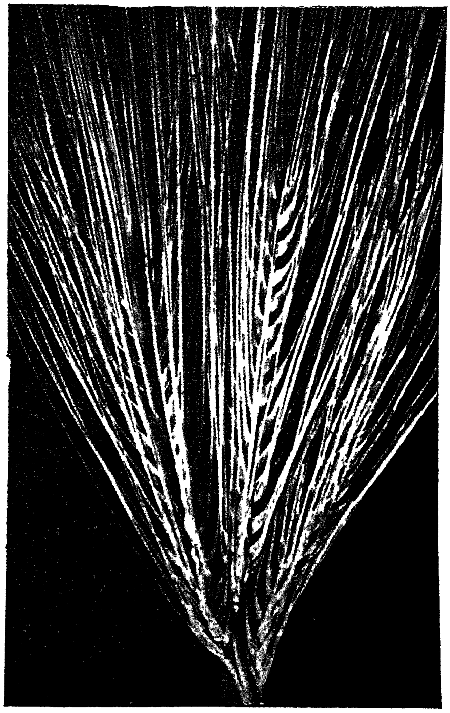


FIG. 151.

Lager beer (*see later*) was prepared as early as the thirteenth century, and its use has since been greatly extended in various countries.

In England the manufacture has flourished since the fifteenth century, the famous porter being first made at the beginning of the eighteenth century.

The improvements made in brewing operations by the introduction of scientific methods have led to a very considerable development of the industry in Germany and elsewhere.

The prime materials for the manufacture of beer are barley, rice, maize, &c., hops, water, and yeast.

1. A. BARLEY [1] should satisfy the following requirements:

[1] Barley (botanical species *Hordeum*) used for making beer is of two types: *two-rowed* (Fig. 150), in which the corns are arranged in the ear in two rows, one on each side, and *six-rowed* (Fig 151), in which there are three rows of corns on each side of the ear. Different kinds of barley can, to some extent, be recognised by the form of the small *basal bristle* found at the base of the corn inside the longitudinal furrow. The value of barley for brewing purposes is largely influenced by the nature of the soil, climate, methods of cultivation, and manuring. Barley is cultivated in all countries and in all climates—in Holland and also in Sicily. It is difficult to keep

(*a*) When moistened and kept at 25° to 30°, 80 per cent. of the corns should germinate in 48 hours and 90 to 95 per cent. in 72 hours.

(*b*) Those are preferred which are heaviest (60 to 70 kilos per hectolitre) and contain about 62 per cent. of starch, about 10 per cent. of protein, and 12 to 14 per cent. of moisture.

(*c*) The skin should be thin and the colour pale yellow, the ends of the corns not being brown.

Barley starch swells at 50°, and with water forms a paste at 80°. With diastase it begins, unlike potato starch, to saccharify as soon as it is completely transformed into paste.

B. Wheat is sometimes used, together with barley, for *pale beers*.

C. Maize is used in America after being skinned and degermed, the germ being rich in oil.

D. Rice is used in America and Scandinavia with the barley.

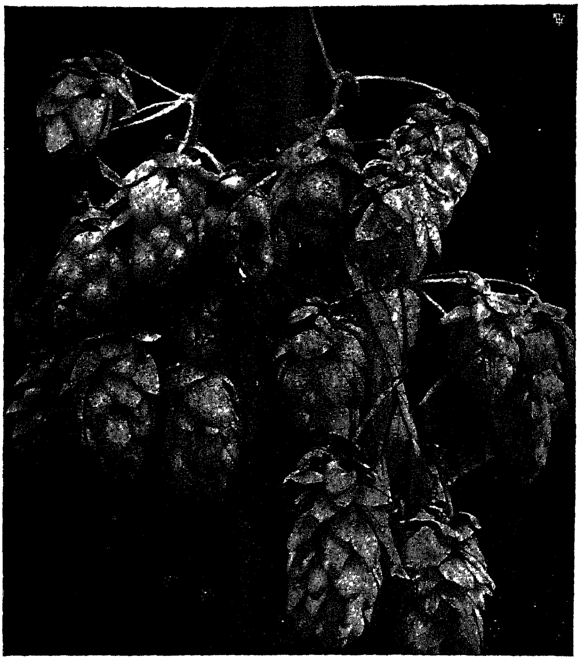


FIG. 152.

2. **HOPS.** The female flowers, dry and mature, of *Humulus lupulus* (Fig. 152) are used, these containing 10 to 17 per cent. of a powder (which can be separated by shaking and sieving) possessing the aromatic and bitter principles which bestow on the beer its aroma and keeping qualities.[1]

varieties pure, since they become modified during growth owing to crossing. Only by the rational system of selection initiated by Dr. Nilsson at the Svalof Institute is it possible to fix different varieties with constant, well-marked characters suited to the various districts in which at one time they originated.

From a commercial point of view, the weight of a barley is of importance and good qualities give a weight of 40 grms. per 1000 corns, or 62 to 67 kilos per hectolitre for thin barleys and as much as 70 kilos per hectolitre for the larger ones. The grains should have a floury and not a vitreous appearance when cut through, and there should be few broken corns as these do not germinate and become mouldy on the malting floor. Germination tests, made on 500 or 1000 corns, should show at least 95 per cent. of germinated corns in 5 to 6 days. With barley harvested under wet conditions, the ends of the corns are darkened.

The *world's production* of barley in 1906 amounted to 315,000,000 quintals; in France, in 1909, 10,800,000 quintals (or 17 million hectols.) were grown on an area of 737,300 hectares; Italy imported 104,000 quintals in 1907, 124,000 in 1908, 176,000 (value £126,120) in 1909, and 178,000 (value £128,120), mostly from Austria-Hungary, in 1910.

[1] The best hops are cultivated in Bohemia (at Saaz), Bavaria, Posen, Wurtemberg, Baden, and Alsace-Lorraine, where they are picked towards the end of August. If they are too ripe the bracts of the hop-cones open and *lupulin* is lost.

The hop should have a yellowish green, and not a brown, colour, and the bracts should not be opened; a too green colour indicates that the hops have been picked in an unripe condition. The seeds have no value for brewing purposes, but the largest hops are of least value. They should not have an unpleasant odour. Since the fresh hops contain 75 to 85 per cent. of moisture, so that they will not keep, it is necessary to dry them in the air or in ovens at 25° to 30° with a strong current of dry air, until they contain only 12 to 15 per cent. of moisture; they will then keep well, even for a year or more. Their keeping qualities may be improved by sulphuring them (with SO_2) either when dry or during the drying. Sulphuring is, however, often applied to inferior hops to mask their defects.

The better qualities are seldom sulphured and, when they are well dried, are kept tightly compressed in large sacks or in evacuated metal cylinders. They may also be kept in a very cool place (cold store).

The bitter flavour and keeping properties imparted by hops depend on their content of α- and β-*bitter acids*, which varies from 6 to 18 per cent. and is determined by Lintner's method as follows: 10 grms of an average sample of the hops are heated in a flask graduated at 505 c.c., with 350 c.c of light petroleum (b pt. 30° to 50°) for six hours on a water-bath at 40° to 45°, an efficient reflux condenser being fitted to the flask. When the latter is cold, it is filled to the mark with light petroleum and shaken, the contents then being filtered. 100 c.c. of the filtrate, mixed with 80 c.c. of alcohol, are titrated with a decinormal potassium hydroxide solution in presence

3. WATER. Formerly water for brewing purposes was invested with a mysterious importance, but nowadays the water is tested in a much more rational and rigorous manner. Preference used to be given to moderately soft water, but now waters of medium hardness are regarded as best, as it is found that a certain quantity of calcium sulphate aids fermentation ; but if the water is too hard, less extract is obtained from the malt and hops. Iron is also harmful, and especially so are waters contaminated with bacteria.[1]

The principal operations in the manufacture of beer are as follow :

(1) CLEANING OF THE BARLEY, to remove dust, soil, stones, damaged and light corns, &c. by means of sieves, fans, &c.

(2) STEEPING OF THE BARLEY for 2 or 3 days in water at 11° to 12° in order that it may absorb the water necessary for germination.

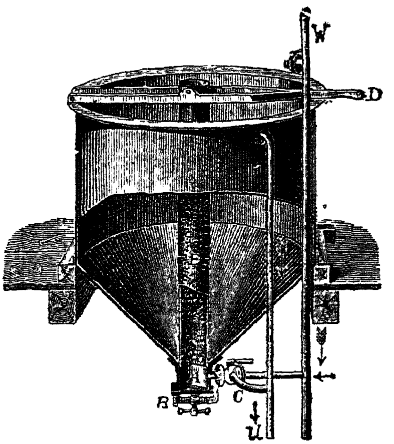


FIG. 153.

For this purpose use is generally made of the Neubecker tank (Fig. 153) made of iron plates, open at the top and cone-shaped at the bottom. In the middle is a wide perforated pipe, *E*, which is surrounded by the barley (500 to 3000 kilos). The water is supplied by the pipe *W*, and is discharged through the perforations of *E*, thus covering the barley ; it is then discharged from the top of the tank through the pipe *U*, the lighter floating corns being carried away. After 7 or 8 hours the water is run off through the tap *C*, and the moist barley left exposed to the air for 5 or 6 hours. Fresh water is then introduced and left for 10 to 12 hours, after which it is run off and the grain exposed for 5 or 6 hours, and so on. This procedure is continued for 30 to 50 hours in summer or 70 to 100 hours in winter, the corns having in that time absorbed about 40 per cent. of water. Steeping of the barley in lime-water has been suggested as a means of preventing abnormal fermentations (Windisch, 1901). In some cases steeping is preceded by washing the barley in running water in rotating cylinders ; or else compressed air is forced into the steeping vessels at frequent intervals, so as to stir the barley. The

of 10–15 drops of phenolphthalein solution. If much fat is present an aliquot part of the light petroleum solution is evaporated and the residue extracted with methyl alcohol, which does not dissolve the fat and, on evaporation, gives the bitter acids ; these can then be weighed.

The quality and commercial value of hops are influenced largely by the nature of the soil and the quality of the manure used, as well as by the variety of the hop itself.

Chemical composition does not always give satisfactory indications for judging of the value of hops, and this is almost always done by men experienced in valuing hops. Hops give up to alcohol 22 to 30 per cent. of extract, about two-thirds of which is composed of a resin giving the bitter flavour and acting as an antiseptic towards certain bacteria injuriously affecting the keeping of the beer, although it has no influence on the yeast. The flavour of the beer is also considerably affected by the tannin contained in the hop to the extent of 2 to 4 per cent.

The determination of the ethereal extract is also employed in judging of the quality of hops ; with good qualities, after evaporation of the ether, 27 to 28 per cent. of residue is left (*see above*, Lintner Test).

The total area of the earth's surface under hops in 1909 was 97,421 hectares (of which 29,000 hectares in Germany) and the production varied from 10 to 15 quintals per hectare. Germany imported 28,000 quintals of hops in 1908 and 36,360 in 1909, but exported 124,000 quintals in 1908 and 88,000 in 1909. The hops imported by the United States were valued at £247,200 in 1910 and at £427,400 in 1911, and those exported at £461,400 in 1910 and at £851,600 in 1911.

[1] The compositions of various waters are as follows

	Good	Medium	Bad	
Dry residue	250–450	450–550	550–700	Parts per million
Ferric oxide and alumina (Fe_2O_3, Al_2O_3)	0–1·5	1·5–2·5	3	
Lime (CaO)	120–150	150–200	200–300	
Magnesia (MgO)	20–50	50–80	80–120	
Sulphuric acid (SO_3)	20–60	60–80	100–200	
Ammonia	—	—	trace–1·5	
Nitrates	—	0–0·5	0·5–1·5	
Organic matter (as oxygen absorbed)	0·4–1·5	1·5–2·0	2–3	
Hardness (French degrees)	15–25	25–35	35–50	
Number of bacteria per 1 c.c.	50–500	500–4000	4000–10,000	

These numbers are only indicative and must not be taken too strictly.

steep-water becomes yellowish brown and acid, and after some time undergoes lactic and butyric fermentations. At the end of the operation, the barley is discharged through the lower aperture, *A*, by undoing the screw, *B*, and raising the tube, *E*, by means of the lever, *D*.

(3) GERMINATION OF THE BARLEY. The steeped barley is carried to the spacious *malting floor*, which is fitted with numerous windows to allow of the renewal of the air when desired, and is arranged so that the temperature can be maintained constant at 15° to 20°. On the impermeable floor (of cement or asphalte), the barley is spread out in a layer 50 to 60 cm. deep, and on the second day the mass is moved with wooden shovels so as to reduce the depth to 30 to 35 cm., this being further reduced to 15 cm. on the third day. Every 8 or 10 hours the grain is turned, the floor being kept well ventilated. The temperature gradually rises, but should not be allowed to exceed 20°; if necessary it can be modified by turning more often and thinning out the barley. After the second day the radicles begin to sprout and later the plumule. In eight to ten days the rootlets become twice or three times as long as the corn and the transformation of nitrogenous material into diastase is at its maximum (Fig. 154 shows the various stages in the germination of barley). The germination should then be interrupted so as not to lose any part of the diastase formed, the *green malt* then containing about 40 per cent. of moisture. A floor of 20 sq. metres is sufficient for only 1000 litres of steeped grain. If the *piece* dries too much, it is moistened by sprinkling with water. In order to prevent mould-growth when the floor is free, it, and also the walls, are washed with 1 per cent. calcium bisulphite solution, the floors being then well dried by ventilation.

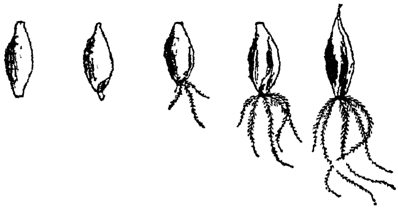


FIG. 154

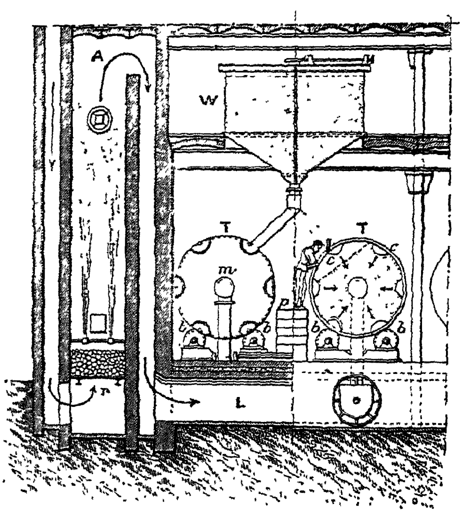


FIG. 155.

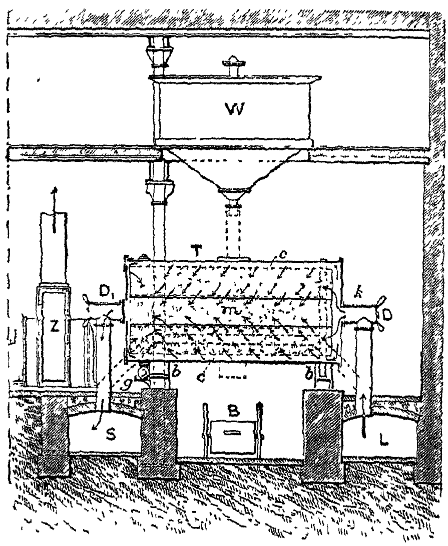


FIG. 156.

The germination is now sometimes carried out on the *pneumatic system*, use being made of the Galland apparatus (Figs. 155 and 156), which consists of a double sheet-iron drum, *T*, rotated by means of the wheels *b* (one rotation in forty minutes). The inner drum is perforated and is filled to the extent of four-fifths with barley from the steeping tank, *W*; along the axis of the cylinder passes a pipe which is also perforated. Air sucked in by a fan, *Z*, is moistened in *A* by means of pulverised water, and from *L* passes into the jacket of the drum, then through the perforations and the grain to the central pipe, *m*. Thence it proceeds to *S*, and so through the fan *Z* to the shaft; a thermometer here shows the temperature of the air, and if this becomes too high the speed of the fan

is increased. If 100 kilos of barley are taken and the air enters at 12° and issues at 20°, 4500 cu. metres of air are required per hour ; if the air is to leave at 16°, 10,000 cu. metres per hour are necessary. The germination lasts 8 to 9 days.

To stop the germination, a current of dry air, heated to 22° to 25° or mixed with gas rich in CO_2 (to diminish the supply of oxygen), is supplied ; in a short time the moisture content of the grain is reduced from 40 per cent. to 20 to 25 per cent.

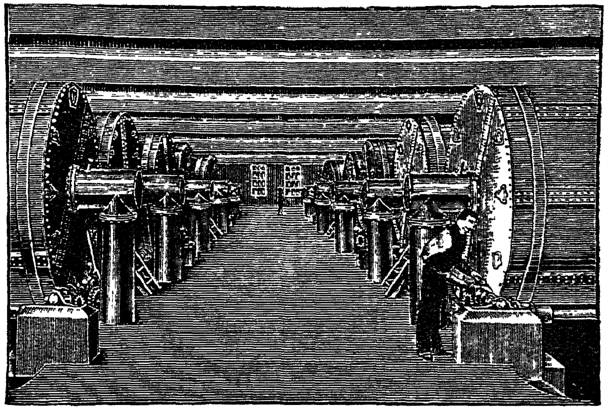


Fig. 157.

For a malting to give continuously 2000 to 5000 kilos per day, three to four steeping-tanks are used, these feeding six to eight Galland drums arranged in batteries (Fig. 157) ; 6 to 10 horse-power are required for turning the drums, driving the fans, &c.

The water necessary for steeping amounts to about 10 to 12 times the weight of the barley, rather less being required to moisten the air for pneumatic malting. The steep-water can hence be used again for the latter purpose if at any time the water-supply is scarce.

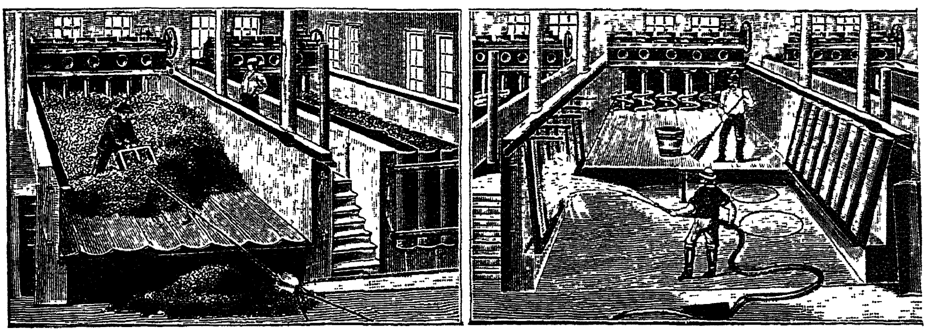


Fig. 158.

Another system of malting, used especially in France, is that of Saladin (shown in perspective in Fig. 158, while Fig. 159 shows a longitudinal section of one of the vessels and Fig. 160 a transverse section of the vessels). There is one vessel, made of concrete

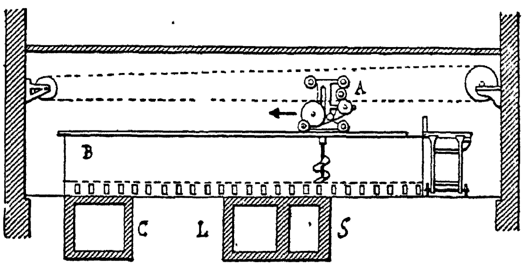


Fig. 159.

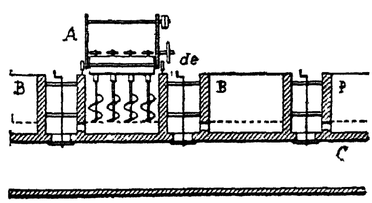


Fig. 160.

and fitted with a perforated false bottom of sheet-iron, for each day that the germination lasts. These vessels, *B*, communicate under the false bottom with a channel containing a fan which draws moistened air through the mass of barley in the vessel (50 cm. deep).

Above each vessel is a mechanical turner, *A*, with a number of screws which rotate in the barley as the turner passes along the vessel. The turner can be transported from one vessel to another and is put into operation twice a day at first (the temperature of the barley being 12° to 14°), then four times a day (at 15° to 18°), and finally twice a day (at 18° to 50°). In some maltings a saving is effected by operating the fan only at intervals—when the temperature rises. Dry air, drawn along the channels, *S*, is finally passed through the malt.

The advantages of the various mechanical processes over the old system of malting are that they can be worked continuously and at any season of the year, while they occupy less space, allow of efficient regulation of temperature, economise labour and general expenses and diminish the percentage of waste.

(4) KILNING OF MALT. The germinated barley is too moist to keep sound, and as breweries require large stocks of malt this must be dry and capable of being kept. If the moisture is reduced to 6 per cent. by air alone the germination process is stopped, and on subsequently raising the temperature to 60° a slight diastatic saccharification occurs, this being greater in amount if the moisture is kept at 12 to 15 per cent.; beyond 70° the diastase is destroyed and certain substances formed which give good flavour, aroma and fullness of taste to the beer and at the same time furnish food for the yeast. When the temperature exceeds 100° part of the maltose is caramelised—for the making of *dark beers*—and a considerable amount of nitrogenous substances, which would cause the beer to keep badly, thrown out of solution.

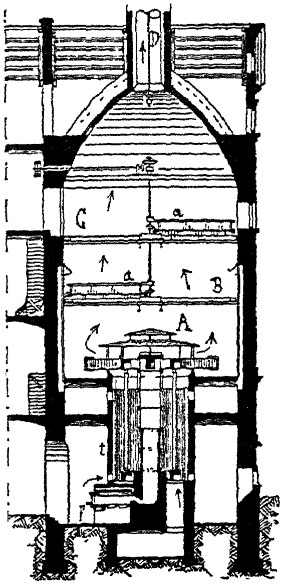


FIG. 161.

In order not to destroy too much of the diastase and to make malt suitable for *pale beers* the drying must first be conducted with warm air. When the proportion of moisture has reached 5 to 6 per cent. the diastase can withstand a temperature of 60° to 70° without losing much of its activity; whilst if the malt is heated when it contains too much moisture (15 to 20 per cent.) the diastase is rapidly destroyed. The drying is carried out in a current of warm air (or of air mixed with the hot gases from a coke or anthracite fire), which passes through the green malt placed in layers 15 to 20 cm. deep on wire or tile floors, often arranged one above the other. Above the upper floor is a chimney, which increases and facilitates the draught started by suitable fans. The air is heated by passing directly over a fire or through batteries of tubes heated in the usual way. During the drying the malt is turned by a suitable mechanical device, at first every 2 hours and later on continuously. The temperature of the air gradually rises, during the course of 84 to 90 hours, by 30° to 35° (during the first few hours germination still proceeds feebly, causing increase in the diastase), and ends at 100° to 110° (for dark beers). Drying is usually effected in less than 48 hours, and it is only beyond 80° that the diastase partially loses its saccharifying properties (at 90° it loses 50 per cent. and at 100° 85 per cent.); this loss is, however, an advantage, since a too highly diastatic malt leads to excessive saccharification and hence to increased attenuation in the subsequent fermentation, so that the beer tastes less full. The peptases also are destroyed beyond 90°, so that the nitrogenous substances are dissolved to a less extent and the beer hence keeps better.

Fig. 161 shows diagrammatically a section of a two-floor malt-kiln in which the air is heated in the tubing, *t*, surrounding the ducts carrying the hot fumes from the coal burning on the grate, *F*. The hot air then traverses the malt on the floors, *B* and *C*, and issues from the chimney, *D*, the turning apparatus, *a*, being kept in motion meanwhile. To obtain 100 kilos of dry malt in 24 hours (maximum temperature 90° to 100°) 20 kilos of coal are required. For making *dark beers* of the Munich type part of the kilned malt is further roasted at about 200° in suitable rotating iron cylinders heated by direct fire; this treatment leads to the formation of caramel, which colours the beer, the malt being then called coloured malt. The temperatures on the malting floors and kiln are registered by auto-

matic devices which construct diagrams showing the temperature at any particular moment.

Nowadays malt for *pale beers* is sometimes heated only to 25° to 30°.

The kilned malt leaves the kiln with 2 to 5 per cent. of moisture and is then cooled and stored in silos or large bins. A malt kept for only 1 or 2 months is to be preferred to an older one.[1]

[1] The *commercial value of a malt* is determined largely by its yield of *extract*, which is measured as follows: 45 grms. of ground malt are placed in a tared flask with 200 c.c. of water, the temperature being kept at exactly 45° for half an hour and then raised 1° per minute up to 70°, this temperature being maintained until the liquid no longer gives a blue colour with iodine; the time required at 70° to reach this point is noted (*saccharification test*). The mass is then cooled and water added to bring its total weight up to 450 grms.; after mixing and filtering through a dry filter, the density of the liquid is determined at 15° and by Windisch's or Schulze's tables the corresponding quantity of extract deduced. The latter can also be obtained from Balling's tables (*see below*), note being taken that they yield low values, the deficit being 0·08 grm. per cent. for specific gravities up to 1·01, 0·345 for specific gravities up to 1·05; 0·48 for specific gravities up to 1·06; and 0·4 for specific gravities up to 1·08. If the maltose is to be determined directly, 10 grms. of the filtered saccharine liquid (corresponding with 1 grm. malt) are diluted to 100 c.c., various quantities of this liquid being then titrated with Fehling's solution, 1 c.c. of which corresponds with 0·0075 grm. of maltose.

C. Lintner (1886–1908) has modified the Kjeldahl method for determining the *diastatic power of malt* as follows: 25 grms. of the ground malt are extracted for 6 hours with 500 c.c. of water at the ordinary temperature, the mixture then being filtered; 2 c.c. (for pale malts) or 8 c.c. (for dark malts) of the filtrate are added to 100 c.c. of 2 per cent. soluble starch solution and the mixture left for exactly half an hour, at the end of which time 10 c.c. of caustic soda solution are added. Into a number of test-tubes, each containing 5 c.c. of Fehling's solution, are introduced varying quantities of the saccharified starch solution (*e.g.* from 1 to 6 c.c.); the tubes are next immersed for ten minutes in a boiling water-bath and then taken out, and the precipitated cuprous oxide allowed to settle; it can then be seen in which of the tubes the Fehling's solution is just completely reduced and in which it is just not reduced. A more exact result can be obtained by using quantities of the saccharified starch solution intermediate to those corresponding with these two tubes. When 0·1 c.c. of the cold water malt extract, acting for one hour on 10 c.c. of 2 per cent. soluble starch solution, forms just sufficient maltose to reduce 5 c.c. of Fehling's solution, the malt is said to have the diastatic power 100; if 0·2 c.c. of the malt extract is required, the diastatic power is taken as 50, and so on.

BALLING'S TABLE

Sp. gr. at 17·5°	Degrees Balling or grms. of saccharose per 100 grms. liquid	Sp. gr. at 17·5°	Degrees Balling or grms. of saccharose per 100 grms. liquid	Sp. gr. at 17·5°	Degrees Balling or grms. of saccharose per 100 grms. liquid	Sp. gr. at 17·5°	Degrees Balling or grms. of saccharose per 100 grms. liquid
1·0010	0·250	1·0210	5·250	1·0410	10·142	1·0610	14·904
1·0020	0·500	1·0220	5·500	1·0420	10·381	1·0620	15·139
1·0030	0·750	1·0230	5·575	1·0430	10·619	1·0630	15·371
1·0040	1·000	1·0240	6·000	1·0440	10·857	1·0640	15·604
1·0050	1·250	1·0250	6·244	1·0450	11·095	1·0650	15·837
1·0060	1·500	1·0260	6·488	1·0460	11·333	1·0660	16·070
1·0070	1·750	1·0270	6·731	1·0470	11·571	1·0670	16·302
1·0080	2·000	1·0280	6·975	1·0480	11·809	1·0680	16·534
1·0090	2·250	1·0290	7·219	1·0490	12·047	1·0690	16·767
1·0100	2·500	1·0300	7·463	1·0500	12·285	1·0700	17·000
1·0110	2·750	1·0310	7·706	1·0510	12·523	1·0710	17·227
1·0120	3·000	1·0320	7·950	1·0520	12·761	1·0720	17·454
1·0130	3·250	1·0330	8·195	1·0530	13·000	1·0730	17·681
1·0140	3·500	1·0340	8·438	1·0540	13·238	1·0740	17·909
1·0150	3·750	1·0350	8·681	1·0550	13·476	1·0750	18·136
1·0160	4·000	1·0360	8·925	1·0560	13·714	1·0760	18·363
1·0170	4·250	1·0370	9·170	1·0570	13·952	1·0770	18·590
1·0180	4·500	1·0380	9·413	1·0580	14·190	1·0780	18·818
1·0190	4·750	1·0390	9·657	1·0590	14·428	1·0790	19·045
1·0200	5·000	1·0400	9·901	1·0600	14·666	1·0800	19·272

Correction of Degrees Balling for Various Temperatures

Determination made at temperature of	Correction of degrees Balling	Determination made at temperature of	Correction of degrees Balling	Determination made at temperature of	Correction of degrees Balling	Determination made at temperature of	Correction of degrees Balling
Deg.		Deg.		Deg.		Deg.	
4	− 0·43	11	− 0·22	17·5	—	24	+ 0·27
5	− 0·40	12	− 0·19	18	+ 0·02	25	+ 0·32
6	− 0·37	13	− 0·16	19	+ 0·05	26	+ 0·37
7	− 0·34	14	− 0·13	20	+ 0·09	27	+ 0·42
8	− 0·31	15	− 0·10	21	+ 0·13	28	+ 0·48
9	− 0·28	16	− 0·06	22	+ 0·17	29	+ 0·54
10	− 0·25	17	− 0·02	23	+ 0·22	30	+ 0·60

Malt kilned with fumes direct from a coal fire communicates to the beer a certain flavour from the smoke. Also, when coal is employed which contains arsenic, the latter becomes deposited on the malt and hence finds its way into the beer. Arsenic may also be present in the glucose often used in brewing; in this case it is introduced by the employment of arsenical sulphuric acid in the manufacture of the glucose from starch.

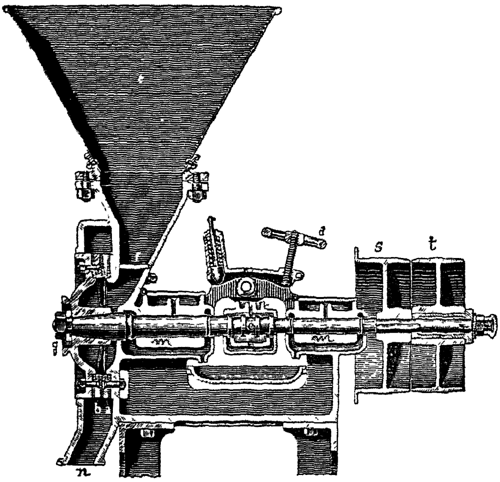


FIG. 162.

(5) CLEANING AND GRINDING. Before the malt is mashed it is freed from dust and rootlets by means of rotating drums of metal gauze (a kind of sieve) furnished with fans. It is then ground but not too finely, the husks being kept whole as far as possible, since they serve in the subsequent operations as filtering material; if the malt is ground too fine it cannot be exhausted, as the liquid will not drain off. A suitable form of mill is the Excelsior Mill, made by Messrs. Krupp (Figs. 162 and 163). The shaft, *g*, fitted with fast and loose pulleys, *s* and *t*, can be shifted from right to left or *vice versa* through the stuffing-boxes, *m*, by means of the lever, *d*. One toothed disc, *a*, is fixed, whilst the other, *b*, rotates with the axis, *g*, and is so adjusted that the teeth pass through the tooth spaces of the other disc. The barley from the hopper, *f*, falls between the two discs, where it is ground, the ground malt (*grist*) being discharged at *n*. For the sake of economy the discs are toothed on both faces, so that when one face is worn the other can be used.

The total loss in weight suffered by the barley during steeping, germination, kilning, cleaning, and grinding amounts to about 20 per cent.

(6) MASHING. This consists in subjecting the ground malt to the action of warm water so that the diastase may act on the starch and convert it into soluble products. The temperature at which the maximum extract is obtained is about 65°, whilst at 55° the starch is only very slightly attacked by diastase, and above 70° diastase loses its saccharifying properties very largely and the wort filters through the grains (husks; *see later*) with difficulty—this effect is aggravated by coagulation of part of the proteins. The quantity and quality of the water have an influence on the mashing, the presence of calcium sulphate facilitating the formation of maltose and maltodextrins and increasing the amount of nitrogenous substances dissolved. From 1 quintal of malt 2 to 3 hectols. of beer are made.

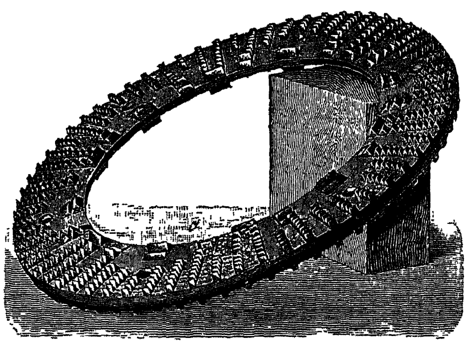


FIG. 163.

There are two systems of mashing: the **infusion** method (at 65° to 72°), used only in top-fermentation breweries, and the **decoction** system, used for bottom-fermentation and sometimes for top-fermentation beers, and with highly diastatic malt or when unmalted barley is used with the malt.

(I) The **infusion process**, used largely in England and Scotland, less in France and still less in Germany, is usually carried out in one of two ways: (i) *rising infusion*, where the malt is first mixed to a paste with 10 per cent. of cold water and then with hot water in the ratio of two parts of water to one part of malt, so that a temperature of 40° is attained. To raise the temperature of 1 kilo of malt (which has a specific heat of about

0·5) from 20° to 40° requires 10 Calories, which can be supplied by 2 litres of water at 45°, the latter falling to 40° on losing 10 Calories ; owing, however, to unavoidable loss of heat, water at 48° to 50° should be used.

This mixing is done in a circular mash-tun of metal or wood, furnished with a perforated false bottom several centimetres above the true bottom, in which are fitted the pipes supplying the hot water (Fig. 164). The mashing and subsequent mixing are effected by efficient mechanical stirrers or rakes.

As soon as the mash has reached the temperature of 40° water at 80° is gradually introduced, the temperature being raised to 63° to 65° in half an hour. It is next mixed for 60 to 70 minutes, the liquid being then discharged by opening the taps under the false bottom so that the liquid passes through the grains and is conducted to the copper. The residue in the tun is mixed for 15 minutes with water at 75°, the liquid being run off and the grains finally washed with water at 80°, all these extracts passing to the copper. In this way almost complete saccharification is attained and the subsequent fermentation produces considerable attenuation. If a less attenuation is desired, either a higher temperature (72° to 73°) is used in place of 65°, or high-dried malt is used.

(ii) *Descending infusion*, which is rarely used, consists in bringing the mass directly to a temperature of 65° to 70° with very hot water and then allowing it to fall slowly to 35° to 40°.

Neither of these methods admits of the use of rice or maize, the starch of which is attacked by diastase only after it has been heated with water to 80° to 85°. Hence with such material the decoction process is used.

(II) **Decoction Process.** This is largely used in North Germany, Austria, and Belgium, and allows of the use of unmalted barley, rice, maize, wheat, &c.

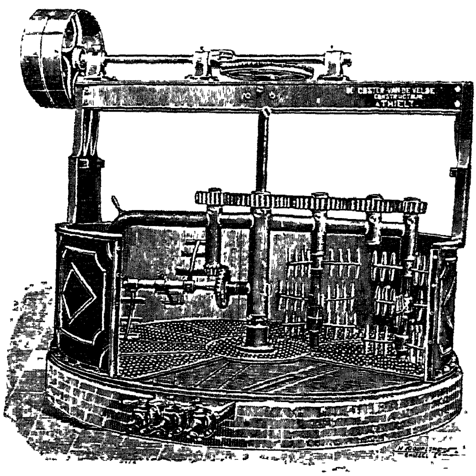


Fig. 164.

The malt grist is first mixed to a paste with cold water so as to dissolve the diastase, this being carried out in a metal vessel without a false bottom ; by the addition of small quantities of boiling water the temperature of the mass is raised gradually to 35°. From one-third to one-half of the turbid wort (*Dickmaische*) is transferred to a double-bottomed copper heated with steam. In many cases coppers with direct-fire heat are used, these being furnished with chains which scrape on the bottom and so prevent caramelisation of the mass which settles (Fig. 165 shows a complete decoction or infusion plant). The wort transferred to the copper is boiled for 20 to 40 minutes and is then returned to the original tun, where it raises the temperature to about 55°. Another one-third or one-half is similarly removed, boiled, and returned, the temperature being thus raised to 65° ; the saccharification has then reached a maximum and the mash become thinner. The complete disappearance of starch is controlled by the reaction with iodine. About one-half of the wort is again removed, boiled, and returned, the temperature being thus raised to 75°. During all these operations continual stirring is maintained. The greater the number of decoctions made the greater will be the density of the wort and the darker the beer. The turbid wort is either allowed to deposit in tuns with false bottoms as shown in Fig. 164, or passed through filter-presses (*see* Sugar Industry) to clarify it, the *grains* remaining in the form of cakes being well washed.[1]

When considerable quantities of other cereals are to be used with the malt use

[1] The *grains* are composed of the whole of the husks of the malt—coagulated proteins, pentosans, fat, maltose and dextrin. They serve as excellent cattle-food, but if not consumed in the course of 24 hours, they undergo change ; they may, however, be placed in silos and dried in a suitable apparatus (*see* Fig. 149, p. 154). *Wet grains* contain 70 to 80 per cent. of water, 4 to 6 per cent. of protein, 1 to 3 per cent. of fat, 8 to 14 per cent. of extractive substances, 1 to 3 per cent. of ash, and 3 to 9 per cent. of cellulose. *Dried grains* contain 6 to 18 per cent. of water, 17 to 26 per cent. of protein, 4 to 9 per cent. of fat, 35 to 55 per cent. of extractive substances, 3 to 12 per cent. of ash, and 9 to 20 per cent. of cellulose ; they have a brown colour, a pleasing odour of new bread and a sweet taste ; they make a good food to follow wheat or oat bran.

is made of a Henze pressure apparatus, as described under Distilling (Fig. 104, p. 119).

The wort thus obtained is boiled with a certain quantity of hops until a certain amount of concentration has been effected. This boiling finally destroys the diastase, intensifies the colour of the wort and aerates it, and oxidises various substances producing acid bodies ; it completely sterilises the liquid, which is also clarified owing to the precipitation of nitrogenous substances, partly by the tannin of the hops.

The *decoction of the hops* is carried out in a separate vessel, the boiling liquid being continually circulated until the hops are exhausted. The decoction is then added to the boiling wort, principally towards the end of the operation ; if added earlier the hop extract loses some of its aroma. The direct addition of the hops to the copper is still used, although the method is not a very rational one ; it is better to pass the boiling wort from time to time into a separate vessel containing the hops and then back to the copper, this procedure being repeated until the hops are exhausted.

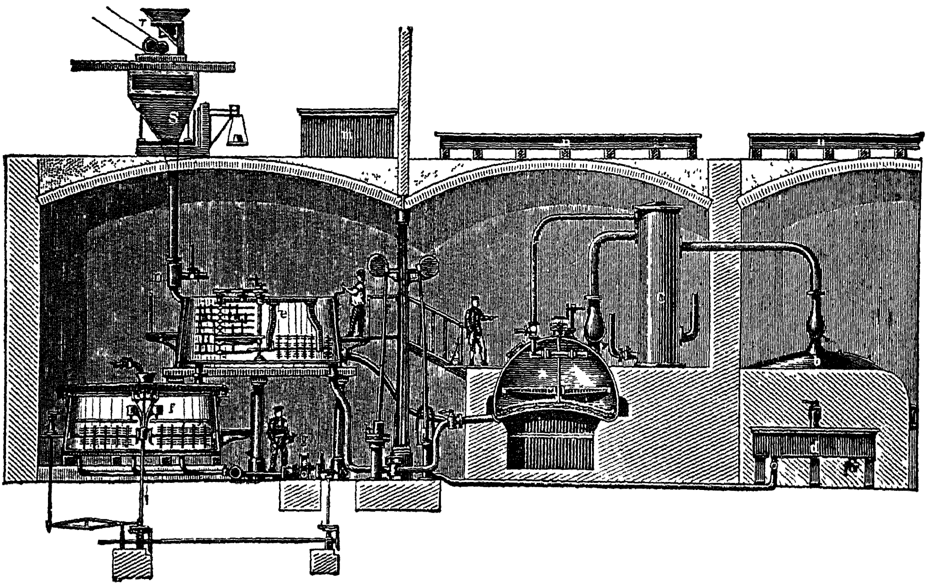


FIG. 165.

In general, 400 to 500 grms. of hops are used per hectolitre of beer, or 2·5 to 5 kilos for every quintal of malt mashed. More hops are usually employed for beers to be kept for some time (*lager beer, stock ale*) than for *draught beer*. The *lupulin* powder contained in the hop gives up resins and essential oils, while the leaves give tannin and the stalks somewhat bitter substances; the whole gives the bitter taste and aroma of the beer, and causes the latter to keep better. A temperature of 75° (Pasteur) is sufficient to sterilise a hopped beer, since the resins have a marked antiseptic action.

The *boiling of the wort* is carried out in copper vessels (*see* Fig. 165, *a*) heated by direct fire or by indirect steam (passed through coils or through the double bottom of the copper), the boiling being continued for 4 to 6 hours with dilute worts (infusion) and only $1\frac{1}{2}$ to 2 hours with the more concentrated decoction worts ; as a rule boiling is continued until the density reaches a certain value for the particular kind of beer to be made (*see later*). The temperature during boiling should be gradually raised and registered. In many modern breweries there are automatic registering thermometers which show the whole course of these operations. When the boiling is finished the wort is allowed to stand for a time, and the Inland Revenue officials then generally make their first measurements (they calculate that 1 kilo of dry malt should give 25 litres of wort with a density of 1° Balling, 5 litres at 5°, &c., an allowance being made of 10 per cent.). The copper is then discharged, the hops being strained off, and the wort pumped to the *cooler*, which is usually at the top of the building. These coolers are large shallow vessels of iron (or copper or wood) in which the coagulated proteins are deposited ; the temperature here is not allowed

to fall below 60° to 65°, otherwise contamination with harmful organisms (butyric, lactic, &c.) might occur. In Italy the tax on the manufacture of beer is calculated from the volume, temperature, and specific gravity of the wort in the cooler (*see later*). The wort is next cooled rapidly by suitable refrigerators to 2° to 3° (for bottom fermentation) or 12° to 15° (for top fermentation). One form of refrigerator which is much used consists of a number of superposed, communicating horizontal tubes (Fig. 166). In the tubes of the upper half water circulates, and in those of the second half brine at a temperature of −6° or −8° from a refrigerating machine (*see* vol. i, p. 231). The wort flows down in a thin skin over the outside of the tubes, meanwhile dissolving an appreciable quantity of air. The cooled and aerated wort flows down to the fermenting vessels placed in cool rooms; for bottom fermentation these are cooled to about 0° by pipes conveying cold brine. The wort from the coolers is turbid and should be filtered through conical cloth bags or filter-presses. In some modern breweries the coolers are omitted in order to avoid any possible contamination (which is, however, difficult with hopped wort at 60°) and the wort is passed direct from the copper to the closed refrigerator and the filter-press, aeration being afterwards effected with air filtered through cotton-wool.

The refrigerators consume considerable quantities of water, and where this is scarce the warm water from the refrigerators is cooled by means of pulverisers or by causing it to flow down over twigs, the evaporation thus caused often lowering the temperature below that of the air (*see* section on Sugar). The boiling of the wort has hence effected a concentration, the preparation of a sterile (aseptic) liquid, and the extraction of the useful principle of the hop, the tannin of which has partially precipitated the proteins. If pale beer is to be brewed the wort can, if necessary, be clarified during the boiling by the addition of a little tannin. During the cooling on the coolers the wort takes up the oxygen necessary for the oxidation of the resins, for clarifying it and, more especially, for aiding the development and multiplication of the yeast during the initial stages of the fermentation

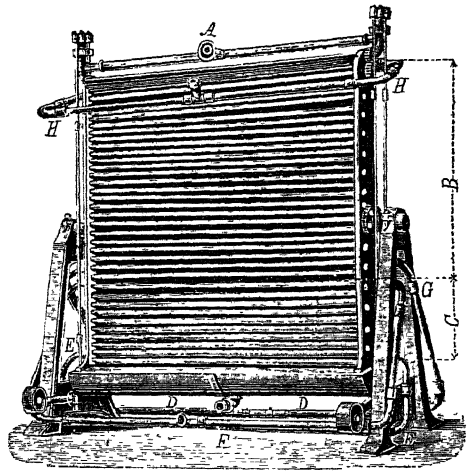


FIG. 166.

Contact of the wort with tin, *e.g.* tinned vessels, is avoided, as turbidity of the beer may be caused thereby, especially if the wort is acid or rich in carbon dioxide.

FERMENTATION. From the density (degrees Balling) or the dry extract of the wort, the *extract* yielded by the materials may be deduced, and, under favourable conditions, the dry extract amounts to about 70 per cent. of the weight of the malt, whilst with bad working it may be as low as 45 per cent. When ready for fermentation the wort contains mainly maltose, malto-dextrins, dextrins, a little saccharose, glucose, and levulose, besides nitrogenous substances partially peptonised and transformed into amino-acids; also lactic acid and potassium phosphates. Fermentation with yeast converts the carbohydrates more or less completely into alcohol and carbon dioxide.[1]

[1] In addition to what has been said on pp. 111 and 123 on ferments and yeasts in general, the following is of interest, especially to the brewing industry.

All yeasts which attack only saccharose, maltose, glucose, and levulose, giving alcohol and carbon dioxide, are *feebly attenuating* yeasts of the so-called Saaz type (*e.g.* the beer-yeasts of Liége, which yield fairly full-tasting sweet beers containing little alcohol). Other yeasts are also capable of fermenting the combined maltose of maltodextrins by means of a special enzyme studied by Delbruck, *maltodextrinase*; these yeasts give the maximum attenuation and form the so-called Frohberg type, producing alcoholic, highly attenuated beers even from weak worts. Between these types—Saaz and Frohberg—there exist intermediate ones giving in 4 days at 25° to 27°, well-defined attenuations in a *normal wort.*

Certain other yeasts are capable of fermenting dextrin combined as maltodextrins, since they contain an enzyme which Delbruck has termed *dextrinase.* Such is the *Schizosaccharomyces Pombé*, separated from the millet beer of the Egyptians. These yeasts constitute the so-called Logos type. *Wild yeasts* are all strongly attenuating and may produce turbidity in finished, slightly fermented beers, which they referment. The yeasts

The concentration of the wort most favourable to the multiplication of yeast is 15° Balling (corresponding with a specific gravity of 1·06).[1] A too dilute wort or one prepared with an excessive proportion of non-germinated grain has not sufficient assimilable nitrogenous food (amino-acids), and this is remedied by the addition of *zymogen*, which is a commercial product. During the period when the yeast develops (first stage of the fermentation) little alcohol and much carbon dioxide are produced.

Two distinct methods of fermentation are in use: *top fermentation*, used generally in England, Belgium, and Holland, and largely in France, and also, at one time, exclusively in Italy; and *bottom fermentation*, usually employed in Germany, Austria, and Denmark, and in general use in countries where beers of the Munich and Pilsen types are made. In hot countries it is easier to regulate bottom fermentation (by refrigeration) than top fermentation, since in summer the temperature of the air is often high enough to have an injurious effect on top fermentation. So that, as a refrigerating plant is necessary, the bottom fermentation system is preferable.

The difference between *bottom* and *top yeasts* is that the latter are covered with viscous, mucilaginous substances and readily stick together and carry bubbles of carbon dioxide developed in the wort to the surface and so produce a rapid fermentation; the former, however, fall to the bottom of the fermenting vessel and, even under the microscope, are not found in large masses. Top yeasts develop well only at temperatures above 12°—best at about 24°—and effect complete fermentation in 4 to 6 days, whilst the bottom yeasts develop below 10° and, after the vigorous primary fermentation of 8 to 12 days at 6° to 8°, continue the maturation of the beer for two or three months by a secondary fermentation at a low temperature (0° to 2°); this procedure gives beers of less attenuation which can be produced or consumed even in summer (*lager beer*). Top-fermentation beers are almost always more highly attenuated, are consumed at once (*draught beer*), and are made more especially in the cold weather; they can, however, be kept, and in some cases stock beers are made on this system.

The advantages and disadvantages of the two processes are as follow:

Top fermentation does not require costly refrigerating plant, and hence lends itself to the construction of small breweries; further, the beer can be sold immediately, and the capital, although small, thus frequently renewed each year. The control and successful working of top fermentation are, however, more difficult owing to ready contamination with numerous harmful bacteria which find at 15° to 20° the most favourable conditions for their development, especially in the summer; in bottom-fermentation beers only yeasts can develop at 0° to 2°.

With top fermentation, in which at first yeasts of the Saaz type and those intermediate to the Saaz and Frohberg types predominate, there develop later bacteria and also Frohberg yeasts (especially during the secondary fermentation), and both of these render difficult the preparation of a clear beer which does not become turbid after fermentation; on the other hand, a bright beer is easily and naturally obtained by bottom fermentation. In summer, then, unless an abundant supply of cold water and also cool cellars are avail-

intermediate to the Saaz and Frohberg types and also Frohberg yeasts themselves are especially active in the secondary fermentation; they increase the apparent fullness of the beer, even when this is light, and maintain a continuous and desirable evolution of carbon dioxide by slowly fermenting the maltodextrins and even dextrins. In order to grow and multiply, yeasts generally require, in addition to carbohydrates and free oxygen, nitrogenous substances, but they cannot make use of nitrates, or ammonium salts, or even the true proteins; they can, however, utilise the decomposition products of the latter, namely, the *amino-acids* (such as asparagine) produced by the proteolytic enzymes secreted by healthy yeasts. They require also mineral substances, *e.g.* calcium and potassium phosphates.

The oxygen of the air is, as has been said, indispensable to the development and multiplication of yeast, and well-aerated worts facilitate the multiplication during the first few days, when only CO_2 and H_2O are produced when, however, the supply of free oxygen diminishes or ceases, the yeast produces more especially alcohol and carbon dioxide. There are also saccharomyces which are solely aerobic and form membranes on the surface of the wort, producing only carbon dioxide and water and destroying the alcohol produced by other yeasts.

[1] The strengths of the worts for different types of beer are. 9° to 10° Balling for *light beers*; 12° to 13° for *draught beers* (Schenkbier); 15° to 20° for *double beers* (Bock or Salvator *beer*); and up to 25° for *table beers*.

able, and rigorous precautions and disinfection are resorted to, it is very difficult to prepare top-fermentation beer, whilst the low temperature required for bottom fermentation can be attained at any season of the year by refrigerating plant. Bottom fermentation gives beers of a more constant type, since the mother-yeast from successive fermentations does not become contaminated so easily as, and hence requires renewal less frequently than, with top fermentation.[1]

When a large amount of yeast is added to a wort the fermentation is initiated and completed more rapidly; with small quantities the same result is obtained, but after a longer time, so that there is more danger of contamination. Usually 250 to 300 grms. of pressed yeast are used per hectolitre of wort—rather more for strong worts.

Especially with top, but also with bottom fermentation, it is most important that all instruments, vessels, and rooms should be kept clean and disinfected. For this purpose boiling water is used and also dilute solutions of hydrofluoric acid, ammonium fluoride, ammonium fluosilicate, calcium bisulphite, and calcium hypochlorite. In all cases, however, great care must be taken to remove the disinfectant completely with abundant supplies of hot water, in order that the yeast may not be injured. Chloride of lime is eliminated by rinsing first with bisulphite solution and then with hot water. Even traces of bisulphite (sometimes added during mashing to prevent the action of lactic ferments) must be completely eliminated, otherwise, during the *alcoholic fermentation, which is a process of reduction,* they may yield hydrogen sulphide and so give a bad taste and odour to the beer. (Bacteria capable of producing hydrogen sulphide sometimes develop in beer.)

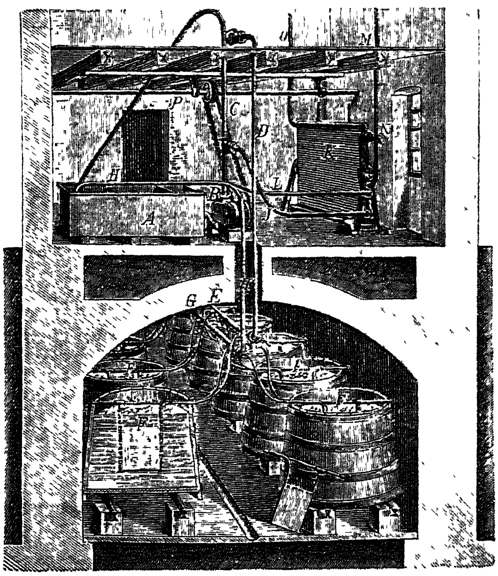


FIG. 167.

Whatever system of fermentation is used, it is always divided into two phases: the *primary* or *vigorous,* and the *secondary.* The primary fermentation begins 12 or 24 hours after pitching, when the yeast has grown to some extent at the expense of the dissolved oxygen, and continues for 3 or 4 days in the case of top fermentation or for 10 to 12 days with bottom fermentation; considerable quantities of carbon dioxide are developed, these forming a dense, white, frothy head on which can be seen brownish spots of hop resin or agglutinated bacteria. In top fermentation, this first head is removed, the next darker one being collected for pitching purposes.

In the bottom fermentation system and in large modern breweries in general, in order that the yeast may be kept as pure as possible, the pitching is carried out in the manner described on p. 127 for distilleries.

[1] With top fermentation, the type and taste of the beer are determined by the united activity of a number of different yeasts and bacteria which are present in given equilibrated proportions, these becoming modified as contamination increases. When the yeast is renewed, the pure yeast naturally gives a different taste to the beer, and this inconvenience cannot be avoided by preparing a mixture of yeasts and bacteria similar to that normally present in the partially contaminated top fermentation. New pure yeasts are less resistant to contaminating surroundings than old ones are.

Attempts are made to-day to keep the fermentation pure as long as possible by the use of good hops, the resins of which exert an agglutinating and paralysing action on the bacteria, so that these can be removed from the tun with the first scum forming on the surface of the fermenting wort; the purer yeast of succeeding heads is then collected for pitching subsequent worts. When the collection of the yeast is delayed, that of the Frohberg type increases. With the object of maintaining the cultures naturally pure and constant, Effront has proposed the addition of *abietinic acid*—a component of *lupulin* and of colophony—to agglutinate and render innocuous the bacteria in fermenting worts (*see also* p. 141). Thus, after elimination of the bacteria with the first scums, purer yeast can be collected and washed with pure water or, better, with water containing a little hydrofluoric acid or ammonium fluoride (5 to 10 grms. per hectolitre), which attacks the bacteria, but not the yeast. It cannot, however, be denied that, in general, washing produces considerable weakening of yeast, which can be reinvigorated by preliminary growth in sterilised, unhopped wort.

During the primary fermentation, a considerable quantity of heat is evolved, and to prevent the temperature exceeding 22° to 25° in top or 7° to 8° in bottom fermentation, *attemperating coils*, through which cold water (top) or brine (bottom) passes, are used to cool the fermenting wort (*F*, Fig. 167). Each fermenting vat is provided with a slate, &c., on which are noted, each day, the temperature and the specific gravity of the wort; the attenuation should reach 58 to 62 per cent. in the primary fermentation and 70 to 75 per cent. in the secondary fermentation, in order that the beers may keep in the warmer rooms of the consumers.[1] When the vigorous fermentation is ended, the head falls and almost disappears, carrying to the bottom of the wort the suspended yeast; in this way the *secondary fermentation* is started, this being allowed to proceed for 15 to 20 days in the trade casks placed in cellars at 10° to 12° (for top fermentation); the beer is then cleared, filtered, and sold. In bottom fermentation, on the other hand, the secondary fermentation is completed in large tuns pitched inside (*see later*); these are not quite filled and are kept for 1 to 3 months in cellars maintained continually at 0° to 2°, where the beer acquires the desired attentuation and its characteristic flavour. The yeast which is deposited in the fermenting vessels can be collected, pressed (p. 125) and sold to bakers or small brewers.

In some breweries the carbon dioxide is now drawn off from the fermenting vats, which are fitted with covers, by pumps and, after being passed through potassium permanganate solution to purify it, the gas is then liquefied (*see* vol. i, p. 382); it can be either utilised in the brewery itself or sold.

The fermenting vessels and the storage casks are constructed of oak or pitch-pine. The use of glass vats has been proposed, as these retain the pure flavour of the beer; such a vat to hold 42 hectols. costs about £40. The cellars have walls and floor of concrete (1 metre higher than the first aqueous border of the subsoil) so that they can be washed when necessary; the roof is of brickwork. These cellars are furnished with draughts to remove the carbon dioxide, with double doors (always on the north side) to prevent the

[1] Determination of the Attenuation and of the Apparent and Real Extracts of Beer. The *apparent extract* is deduced from the density of the well-shaken (to remove CO_2) beer and the corresponding number of degrees Balling (*see* p. 167). The *real extract* is deduced from the specific gravity (and Balling's tables) of the beer freed from alcohol by evaporating it to one-third of its volume and making the residue up to the original volume The original *extract of the wort* may be calculated with moderate accuracy by adding to the real extract the amount of alcohol (determined as in wine, p. 147) multiplied by 1 92.

The *degree of real attenuation* (A) is referred to 1 hectolitre of wort and indicates how many parts per 100 of the *extract* of the wort are transformed into alcohol and carbon dioxide, it is obtained by means of the following formula:

$$A = \frac{D - d}{D} \times 100$$

where D represents the percentage of extract in the wort and d the percentage of *real extract of the beer*.

In practice, the percentage of extract is sometimes replaced by the degrees Balling, but the results thus obtained are not very exact. If we make $D = 15°$ Balling and $d = 5°$, the real attenuation becomes:

$$A = \frac{15\ 5}{15} \times 100 = 66{\cdot}66 \text{ per cent.}$$

But it cannot be denied that Balling degrees refer to kilos of sugar or of extract in 100 kilos of solution, so that a wort showing 15° Balling (sp. gr 1 0615) contains 15 kilos of extract per 100 kilos of wort, or 15·922 kilos (*i.e.* 15 × 1·0615) in a hectolitre of wort; the beer, free from alcohol, showing 5° Balling, has a sp gr. 1·020, and 1 hectolitre contains 5·100 kilos of extract, so that 10·822 kilos of extract have been fermented and the *true attenuation* is $\frac{10\ 822}{15{\cdot}922} \times 10 = 67\ 6\ \%$.

Practical brewers find it more convenient, in considering the degree of attenuation of a wort, to calculate the *degree of apparent attenuation* (A') from the apparent extract of the beer d by means of the formula, $A' = \frac{D-d}{D} \times 100$; for example, a wort of 16° Balling has the sp. gr. 1·0658 and 1 hectolitre contains 17·05 kilos of extract, while the beer, with 7° Balling of apparent extract, has the sp. gr. 1·0281, corresponding with 7 20 kilos of extract per hectolitre. The apparent attenuation is hence $\frac{17{\cdot}05 - 7\ 20}{17{\cdot}05} \times 100 = 57{\cdot}9$ per cent. per hectolitre.

The attenuation can be deduced in a rather less exact manner if instead of degrees Balling are used degrees of the *legal densimeter* (*i.e.* the figures in the second decimal place of the specific gravity, a value of 1·063 for the latter thus corresponding with 6·3° on the legal densimeter). In the above example, 16° Balling corresponds with sp. gr 1·0658, hence with 6·58° on the densimeter; similarly, 7° Balling corresponds with 2 81 densimeter degrees. Hence the apparent attenuation is given by:

$$A' = \frac{6{\cdot}58 - 2{\cdot}81}{6{\cdot}58} \times 100 = 57{\cdot}3 \text{ per cent.}$$

which differs little from the value calculated above from the degrees Balling, and is sufficiently exact for practical purposes. Hence, both for real and apparent attenuation, Balling's tables can be dispensed with, it being sufficient to determine the specific gravity. It should be noted that the legal density expresses the weight of wort contained in the volume occupied by 1 kilo of water measured at 17·5°.

entry of warm air from outside and with electric lighting so that windows, which dissipate the cold may be avoided. The vats and casks are raised 50 to 60 cm. from the ground and are inclined slightly forward so that they can be emptied completely and easily cleaned from outside. Along the ceiling run pipes for the circulation of cold brine (bottom fermentation), which maintain a temperature below 60° in the fermentation cellars and one of 0° to 2° in the lager cellars.

Ten or fifteen days before the beer is run off from the lager vessels—which have been several times filled up to avoid contact of the beer with the air and consequent danger from acetic ferments — the bung-hole is tightly closed so as to supersaturate the beer under slight pressure with carbon dioxide, which is still developed more or less feebly according to the state of maturity of the beer. If a beer contains, say, 0·1 to 0·2 per cent. of CO_2 before the bung-hole is closed, it will subsequently contain six or seven times that proportion.

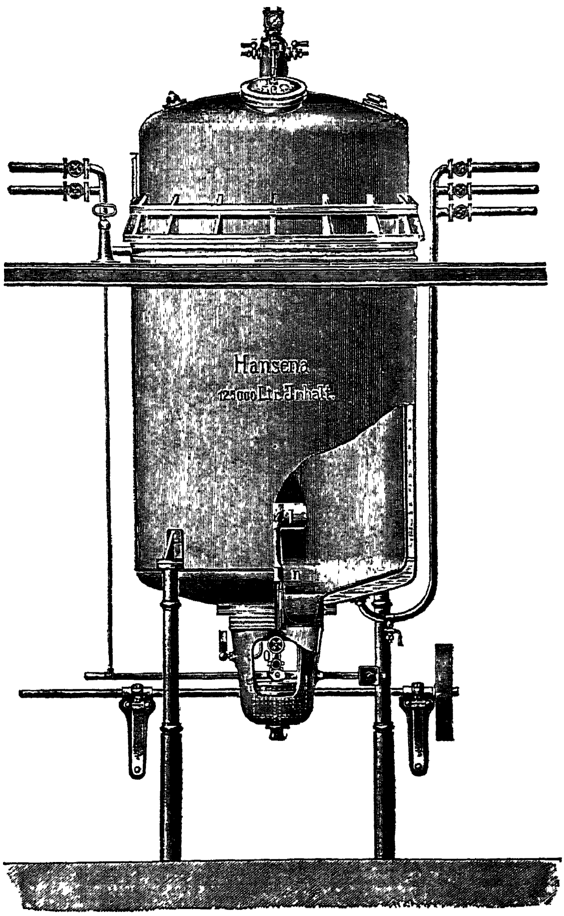


Fig. 168.

Nathan-Bolze Rapid Process (Ger. Pat. 135,539, 1900). This process was tested on an industrial scale in 1904 in the Fermentation Institute at Berlin, and gave satisfactory results. But the application of the process has not progressed as rapidly as was hoped for a process which allows of mature beer being prepared in 8 or 10 days, and works under conditions of sterilisation formerly attainable only in the laboratory or in the manufacture of spirit by the amylo-process (p. 129). The hot, sterile wort from the copper passes into a large hermetically sealed, sterile vessel of enamelled iron (a special resistant enamel being employed) surrounded by an iron jacket through which water can be passed. These vessels have a capacity of 125 hectols. or more and are called Hansena vessels. They are provided with powerful stirrers (Fig. 168), which keep the wort in continual motion during the fermentation and thus accelerate the transformation of the maltose into alcohol and carbon dioxide.

After the temperature of the wort has been lowered to 50° by passing water through the jacket and the diminution of pressure (owing to the condensation of steam) compen sated by the admission of sterilised air, the latter (which has served also to aerate th wort) is replaced by carbon dioxide, the cooling being continued to 10°. The pure yeast is then introduced through suitable pipes, the mass being slightly stirred at intervals of an hour. The gas developed is removed in order to hasten the fermentation, and is washed with permanganate, part of it then being compressed (*see* p. 174). The carbon dioxide which is not compressed is utilised to remove the *new beer* flavour from beer already fermented in the Hansena vessels; the gas is passed in at the bottom (after removal of the yeast sediment) at the ordinary temperature, the mass being continually stirred

meanwhile, it being the carbon dioxide which effects the elimination from the beer of the volatile products to which the disagreeable taste and odour of new beer are due. The gas issues from the top of the vessel, passes to the purifiers and is again conducted through the beer, this process being continued for 10 hours on end. The primary fermentation is finished in less than 3 days, and, after the passage of gas through the beer is completed, the temperature is lowered to 0° and the beer saturated for 24 hours with slightly compressed carbon dioxide. The beer is finally filtered and delivered to the trade casks, where it keeps well even in the hot weather.

Such a process, simple, rapid, and economical (the cost of the beer being diminished by about 2*s* 6*d*. per hectolitre), although it does not give a very delicate flavoured beer, should be suitable to hot countries and to small breweries. Several European breweries already work on these lines and recently (1907) one has been constructed at Milan to employ a modification of the Nathan patent, consisting of a system intermediate to the old process with open fermenting vessels and that devised by Nathan ; in this case enamelled iron vessels are used both for the primary fermentation and for the maturation (3 to 4 weeks). These vessels cost about £1 for each hectolitre of capacity.

If to the Nathan process is added the Meura system of mashing (1891)—which has rendered the preparation of the wort as simple as possible by mashing the finely ground malt in a horizontal cylinder fitted with stirrers so that the mash can be rapidly cooled or heated and wort ready for passing to the filter-press and thence to the copper can be obtained in an hour—it will be understood how the manufacture of ordinary beer has been shorn of those practical and theoretical difficulties long regarded as insurmountable.

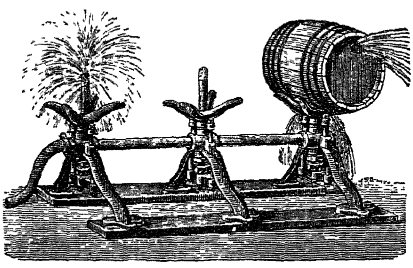


FIG. 169.

RACKING OF BEER. Beer is delivered to the consumer in bottles and in casks, and should be perfectly bright, cold, and supersaturated with carbon dioxide. To render it bright, the old method of clarification with gelatine or of filtration through bags has now been largely replaced by the use of the filter-press, which acts more rapidly and yields brilliant beer. The filtration is carried out in suitable frames through filter-cloths or, better, through finely divided cellulose (such as is used in paper-making) under a pressure of about half an atmosphere. These filter-presses are the same in principle as, and little different in form from, those which are used for the filtration of saccharine liquids and are described in the section on Sugar. (In England, beer in cask is clarified by mixing with the beer a small quantity of *finings*, which consist of isinglass " cut " or dissolved in an acid, such as tartaric, sulphurous, &c. ; these finings are gradually deposited on the bottom of the cask and carry down with them any suspended protein substances, hop-resins, &c.). Bottling is to-day carried out with all the care employed in the preparation of sparkling wines. A few lines may be devoted to the preparation of beer-casks, since the methods employed are peculiar to the brewing industry.

In order that beer for retail consumption may retain its flavour, it must be kept cool and saturated with carbon dioxide up to the moment when it is drawn off into the customers' glasses, and for this purpose the use of liquid carbon dioxide with the arrangement shown in vol. i, p. 389, is well adapted.

RESINING OR PITCHING OF CASKS. The keeping of beer sound depends largely on the cleanliness of its surroundings and of the vessels in which it is stored. Hence the casks, returned empty from the customers, are first well scrubbed and washed both inside and outside with water under pressure by means of automatic plant (Fig. 169), and are then disinfected by means of formalin vapour or other antiseptics, or, better still, by pitching the internal surface with natural or artificial resins, which should be transparent and have a melting-point of about 50° ; in this process, which was first used in Bavaria, and is nowadays largely employed all over the Continent, aromatic resins are no longer used, mixtures of colophony with other residues from the distillation of turpentine being prepared by fusion and then rendered more elastic by the addition of resin oil (10 per cent.). To free the casks from the old resin and coat them again every time they are

returned to the brewery, they are heated inside by means of air supplied from a Roots blower, *B* (Fig. 170), and heated by passing through red-hot coke, the hot air being forced into the casks through the tubes, *D*, for 5 minutes. The old pitch is discharged and the new pitch (about 200 to 250 grms. per hectolitre), fused and heated to 250°, introduced into the sterile cask. The bung-hole is then closed, the cask rotated automatically for a

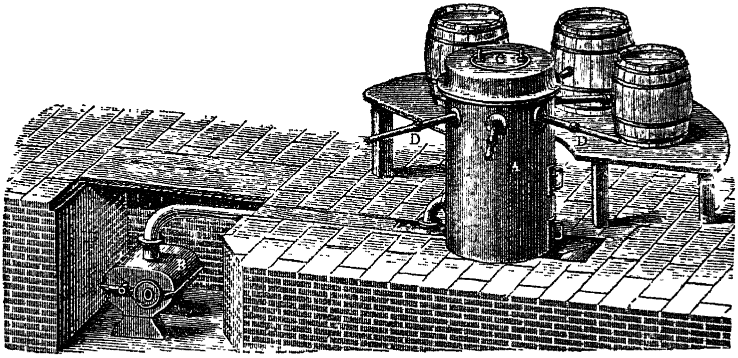


Fig. 170.

few minutes, the excess of pitch poured out, and the rolling of the cask continued until it is cold. The lager-vessels used for the maturation of the beer are treated in a similar way.

PASTEURISATION. Beer, more than wine, is subject to numerous changes and diseases (turbidity due to inferior materials, incomplete saccharification or excess of proteins ; acidity caused by acetic or lactic acid ; stinking fermentation produced by

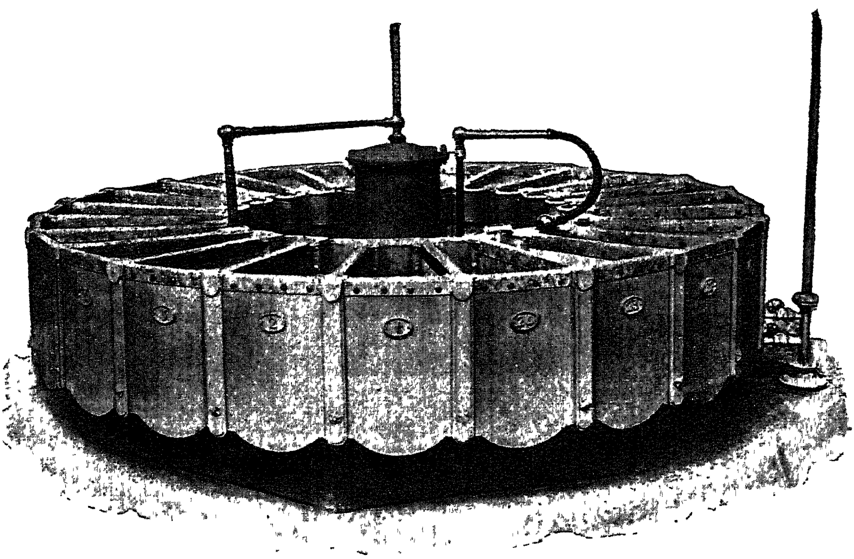


Fig. 171.

various bacteria, &c.), and it is difficult to remedy these inconveniences except by improvement in the methods of working. In order that beer may remain unchanged when kept for a long time in bottle or when sent to hot places, it is advisable to pasteurise it. The bottles are tightly stoppered and placed in vessels containing cold water, which is then *gradually* heated to a maximum of 60° to 65°, this temperature being maintained for 10 minutes ; the vessels should be covered so as to avoid danger from breakages. The water-bath is subsequently allowed to cool *slowly* to the ordinary temperature. Top-fermentation beers are rarely pasteurised, as they sometimes acquire an unpleasant flavour

under this treatment; bottom-fermentation beers, however, undergo no change and keep good even for ten years.

In large breweries, very efficient pasteurising apparatus is employed, the bottles being moved automatically in suitable vessels in which the water moves in the opposite direction.

Of the many improved forms in use at the present time, the Gasquet circular type is shown in Fig. 171. Here the chambers are filled successively with baskets of bottles, which are raised by suitable cranes. The water, at a gradually increasing temperature, is drawn from each chamber by means of a tube communicating with a pump, heated by a central thermo-syphon, and then passed on to the succeeding chamber. A bell rings every five minutes as a signal for the bottles of a cool chamber to be removed and replaced by fresh ones.

The bottles are made of a special glass, which diminishes the proportion of breakages to less than 1 per cent.

ALCOHOL-FREE BEER. A proposal has recently been made to manufacture beer containing no alcohol by treating wort directly at 0° with yeast which has previously been subjected to special treatment effecting the destruction of almost all of the zymase but not that of the peptase and other proteolytic enzymes; the carbohydrates hence give no alcohol, the proteins alone being decomposed. These yeasts remove the flavour of fresh wort, the beer being used before alcoholic fermentation begins (Ger Pat. 180,128).

COMPOSITION AND ANALYSIS OF BEER. The most varied types of beer are found in different countries, and of each type there are usually the two qualities—*pale* and *dark*.[1] The density varies from 1·010 to 1·030, and the amount of alcohol usually from 3·5 to 4·5 per cent. by volume, although export beers often contain 5 to 5·5 per cent. of alcohol, and certain special beers still more. The amount of extract also varies considerably, being as

[1] The compositions of some of the best-known beers are as follow:

	Alcohol	Extract	Ash	Real attenuation
	per cent. by vol.	per cent. by vol.	per cent. by vol.	per cent. by vol.
Pale Berlin beer	3·91	4·85	0·14	60 50
Berlin lager beer	4·00	6 15	0 20	54 70
Export Bavarian beer	4·78	10 67	0 29	45 44
Munich Spaten beer (at Munich)	3 23	6 61	0·28	48 40
,, ,, ,, (at Milan)	5 23	—	—	—
,, Salvator beer	4 64	9 08	0·28	49·00
,, Spaten table beer	7·0	10 35	—	57 40
,, Bock	4·20	7·10	—	54 20
,, white beer	3·51	4 73	—	59 58
Vienna lager beer	3·62	6 01	—	54 50
Pilsen beer	3 47	4 97	—	59 00
North of France beer	3·20	4 04	—	61·20
Amsterdam beer	4 30	7·0	—	36·40
Brussels lambic	5 94	3·30	—	78 00
Belgian faro	4·33	5 1	—	62 80
Bass's pale ale	6 15	6 87	—	64 00
Scotch pale ale	8·50	10 90	—	59 9
Dublin stout	7·23	6·15	—	70 64
London porter	5·40	6 00	—	63 3
American beer	5 89	6 45	—	63 15
Milan beer: Pilsen type	3 92	5·43	0·21	57·91
,, ,, Munich type	3 50	5·58	0 20	54 63
Porretti beer (Varese)	3 98	5·66	0·22	57 45
Italia beer (made at Milan by the modified Nathan-Bolze process)	4 78	6 00	0 22	59 43

The *real attenuation* (or *degree of fermentation*, *see* p. 174) is calculated by multiplying the percentage of alcohol by 1·92 ($= d'$), and adding to this product the extract of the beer, d; this gives the extract, D, contained in the wort prior to fermentation and then the attenuation or percentage of extract fermented $= \frac{D - d}{D} \times 100$.

Some English breweries make stout from a mixture of 65 per cent. of pale malt, 10 per cent. of black malt (for colour), 10 per cent. of caramelised malt and sometimes 10 per cent. of cane-sugar and 5 per cent. of maize This very dark beer is attenuated to a relatively small extent, and retains a full, sweet taste, this being partly due to the almost entire absence of gypsum in and the small total hardness of London water; these beers also contain few hops. Export stout is made from worts having gravities as high as 25° Balling, whilst *porter* is lighter in character. The pale beers of Berlin are made with a good proportion (75 per cent.) of malted wheat.

much as 12 per cent. for certain types of beer; for ordinary beers it lies between 5 and 6 per cent. (1 per cent. being maltose). The proportion of ash is generally less than 0·3 per cent. The amount of carbon dioxide dissolved varies from 0·15 to 0·40 per cent.

The *analysis of beer* is carried out in a similar manner to that of wine (p. 157), but the carbon dioxide is eliminated by heating the beer to 40° and shaking for several minutes before the *specific gravity* and *acidity* are determined; the latter does not exceed 0·3 per cent. and is expressed as lactic acid (1 c.c. N/10-alkali ≡ 0·009 grm. lactic acid) or as cubic centimetres of normal alkali used per 100 c.c. of beer. To avoid frothing during the distillation of the *alcohol*,[1] a little tannin is added. The *nitrogenous substances* are determined on the extract of 40 c.c. of the beer by Kjeldahl's method (p. 10), the proportion of nitrogen being multiplied by 6·25 to give the corresponding amount of proteins. The reducing sugar is determined by means of Fehling's solution and is calculated as maltose (*see* Note, p. 167).[2]

STATISTICS. In Italy the brewing industry has never been in a flourishing condition, owing to the abundance and cheapness of wine—possibly more commonly drunk than water. The beer manufactured from remote epochs in Italy was made by the top-fermentation process and was of poor quality; it did not keep well in summer, was stored carelessly by the retailers and was consumed for only about a couple of months in the year—close to where it was produced. Technical improvements have been introduced tardily, but nowadays the industry is largely concentrated into a few large breweries using the most modern methods and controlled by technical experts from other countries.

About one-half of the beer imported into Italy is supplied by Austria-Hungary, about one-third by Germany, and one-tenth by Switzerland:

PRODUCTION, IMPORTATION, AND CONSUMPTION OF BEER IN ITALY

	Production hectols.	Imports hectols. in cask	Consumption Total hectols.	Consumption Per head litres
1880	116,000	46,900	163,000	0·57
1890	160,900	99,500	260,000	0·86
1894–95	95,500	60,000	156,000	0·50
1900	154,000	54,750	209,000	0·66
1903	185,000	70,000	255,000	0·79
1904	220,000	80,000	300,000	0·92
1905–06	304,000	90,000	394,000	1·20
1906–07	360,000	94,494	455,000	1·50
1907–08	400,000	95,213	495,000	1·60
1908–09	473,000	88,100	561,000	1·80
1909–10	563,000	89,737	651,000	2·00

[1] The proportion of alcohol can be calculated indirectly by means of the formula, $A = (s/S) \div S$, where A indicates the percentage of alcohol, s the specific gravity of the beer, S the specific gravity of the beer freed from alcohol and made up to the original volume; the alcohol Table (p. 148) gives the percentage by weight corresponding to the value of s/S and division of this percentage by S gives the true percentage of alcohol.

[2] The determination of *sulphurous acid* (only traces are allowed in beer) derived from sulphites or sulphurous acid added to preserve the beer, is effected by distilling 200 c c. of the beer, previously acidified with 5 c.c. of syrupy phosphoric acid, in a current of carbon dioxide and passing the distillate through 50 c c. of iodine solution (5 grms. I + 7·5 grms. KI made up to 1 litre with water); the iodine solution is then acidified with hydrochloric acid, boiled to expel excess of iodine and precipitated with barium chloride, the filtered, washed, and ignited barium sulphate being weighed; multiplication of this weight by 1 372 gives the amount of SO_2 per litre of beer. For the detection of *boric acid*, 100 c.c. of beer are evaporated to dryness and the residue calcined; a little sulphuric acid and alcohol are then added to the resulting ash and the mixture ignited and stirred; the appearance of a green colour at the edges of the flame indicates the presence of boric acid. The quantitative determination of boric acid is difficult and is only rarely carried out, Rosenbladt and Gooch's method being then used.

For the detection of *fluorides*, sometimes (although prohibited) added as preservative, 100 c.c. of the beer, rendered alkaline with ammonium carbonate, are boiled, mixed with 3 to 4 c.c. of calcium chloride solution, boiled again for 5 minutes and filtered, the residue being washed and calcined in a platinum crucible. One cubic centimetre of concentrated sulphuric acid is then added and the crucible, covered with a watch-glass partly coated with paraffin wax, gently heated. In presence of fluorides, the glass is attacked in the unprotected parts.

The *degree of attenuation* or of *fermentation* is calculated as indicated in the Note on the preceding page.

Adulteration with *salicylic acid* is detected by acidifying 100 c.c. of the beer with 5 c.c. of hydrochloric acid and shaking with 50 c.c. of ether and 50 c.c. of light petroleum. The ethereal solution is separated and evaporated to dryness, the residue being taken up in water and filtered. If the liquid gives a violet coloration with a little dilute ferric chloride solution and a red one with *Millon's reagent* (aqueous mercuric nitrate containing a little nitrous acid), the presence of salicylic acid is certain.

Saccharin is determined by evaporating an ethereal extract obtained as above, dissolving the residue in a little

The consumption of beer in Italy takes place mostly in the towns of the north and centre, and the average consumption per head in Milan, Turin, or Rome is at least ten times that for the whole country.

The production of beer in Japan was 362,000 hectols. in 1907; 294,100 in 1908; 271,500 in 1909, and 280,000 in 1910.

The production of beer in other countries in 1900 was as follows: Germany, 67,000,000 hectols. or 118 litres (in 1907, 70, and in 1910, 64 litres) per head. England, 59,000,000 hectols. (57,000,000 or 150 litres per head in 1909). Austria-Hungary, 20,000,000 hectols. (72 litres per head) or 19,000,000 in 1909. Belgium, 14,000,000 hectols. (213 litres per head). France 9,000,000 hectols. (25 litres per head; but here, too, the consumption is localised, the annual consumption per head in Lille being 360 litres); in 1909 France produced 11,000,000 hectols. The United States, 48,000,000 hectols. (63 litres per head) in 1900 and 70,000,000 in 1909. Spain, about 1,000,000 hectols., and Russia, 6,200,000 hectols. in 1909.

In 1900, Germany, with 10,000 breweries, produced twice as much beer as in 1880, and in 1885 exported 1,500,000 hectols. One large brewery in Germany makes more beer than the whole of Italy consumes. (Italy has 93 breweries at the present time.)

In 1881, England produced 45,000,000 hectols.; Austria-Hungary, 12,000,000; Belgium 9,000,000; France, 8,000,000; Switzerland, 1,000,000 (now 1,500,000), and the United States, 19,000,000.

The *world's production* of beer in 1910–11 was 271,000,000 hectols.

In Italy the brewing tax was $5\frac{3}{4}d.$ up to 1891, when it was raised to $11\frac{1}{2}d.$ (causing a temporary diminution in the consumption at that time) per saccharometer degree per hectolitre, measured with the decimal saccharometer at 17·5° on the wort from the *cooler*, an allowance of 12 per cent. being made for loss during the subsequent operations; the tax varied from a minimum of 115*d.* to a maximum of 184*d.* per hectolitre, according to the strength of the beer. Imported beer pays 29*d.* more, or the importers can demand the tax to be levied on the extract degrees, these being increased by twice the number of alcohol degrees. The exchequer collected £180,000 in 1905–6 and £211,800 in 1906–1907 as tax of manufacture.

In Germany beer costs about 12*s.* per hectolitre, or rather more with the extra taxation of 1910. In Italy the cost is about 32*s.* (that imported from well-known breweries about 40*s.* per hectolitre).

ALCOHOLS HIGHER THAN ETHYL

PROPYL ALCOHOLS, C_3H_8O. The two isomerides theoretically possible are known:

(1) **Normal**, $CH_3 \cdot CH_2 \cdot CH_2 \cdot OH$ (*propanol*-1 or *ethylcarbinol*). This can be obtained from fusel oil (p. 122) by fractional distillation or from its bromo-derivative. It has an agreeable odour, b.pt. 97°, sp. gr. 0·804, and is readily soluble in water. On oxidation it gives propionic acid, which proves its constitution.

(2) **Sec. or Iso-Propyl Alcohol**, $CH_3 \cdot CH(OH) \cdot CH_3$ (*propanol*-2 or *dimethylcarbinol*), is a colourless liquid, b.pt. 81°, sp. gr. 0 789. It is obtained from isopropyl iodide and hence indirectly from glycerol, or by reducing acetone with sodium amalgam, the constitution attributed to it being thereby confirmed.

BUTYL ALCOHOLS, $C_4H_{10}O$. The four isomerides, predicted by theory, are known:

(1) **Normal Butyl Alcohol**, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OH$ (*butanol*-1 or *propylcarbinol*), is a liquid, b.pt. 117°, sp. gr. 0·810, and has an irritating odour; 12 vols. of water at 22° dissolve only 1 vol. of it, this being separated from the solution by the addition of a soluble salt.

sodium carbonate solution, evaporating in a silver dish and fusing the residue with solid caustic soda; the white mass is dissolved in water, the solution acidified with hydrochloric acid, and the sulphuric acid (derived from the sulphonic group of the saccharin) precipitated quantitatively as barium sulphate. The weight of the latter, multiplied by 0 785, gives the weight of saccharin

Caramel added to colour the beer is recognised by shaking 20 c c. with about 30 to 40 grms (*i.e* until saturated) of solid sodium sulphate and 60 c c of 95 per cent. alcohol. If the lower liquid is markedly coloured and forms a greenish brown deposit, the presence of caramel is indicated; beer containing no caramel becomes decolorised and gives only a greenish or dark greenish brown deposit if it contains coloured malt

Picric acid is detected by evaporating a litre of the beer to a syrupy consistency, extracting with boiling absolute alcohol, filtering and evaporating the alcoholic liquid, dissolving the residue in water, adding a few drops of hydrochloric acid and heating for an hour with a few strands of wool; if the latter are coloured yellow, picric acid is present.

Extraneous *bitter substances* are tested for by evaporating 2 litres of beer to half its volume and precipitating the residue in the hot with lead acetate; the hot liquid is filtered rapidly and the lead then precipitated with ammonium sulphate and filtered off. The filtrate should have no bitter taste.

It is found in fusel oil and can be obtained by fermenting glycerol or mannitol (yield 8 to 10 per cent.) with *Bacillus butylicus* (contained in the excreta of cows). It can also be prepared synthetically by the various general processes (p. 104). Its constitution is indicated by its syntheses and by the possibility of transforming it into normal butyric acid by oxidation.

(2) Secondary Butyl Alcohol, $CH_3 \cdot CH_2 \cdot CH(OH) \cdot CH_3$ (*butanol*-2 or *ethylmethylcarbinol*) is a liquid with an intense, peculiar odour, b.pt. 100°, sp. gr. 0·808. It can be obtained by treating the tetrahydric alcohol, erythritol, $C_4H_6(OH)_4$, with hydriodic acid or by the interaction of normal butylene and hydriodic acid and hydrolysis of the resulting iodide.

(3) Isobutyl Alcohol, $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH \cdot CH_2 \cdot OH$ (*methylpropanol*), is termed also *butyl alcohol of fermentation*, since it abounds in the *fusel oil of potatoes*, from which it can be extracted by forming the corresponding iodo-compound. It is a colourless liquid, b.pt. 107°, sp. gr. 0·806, and has a characteristic alcoholic smell. Its constitution is determined by the fact that, on oxidation, it yields isobutyric acid, the constitution of which is known.

(4) Tertiary Butyl Alcohol, $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C(OH) \cdot CH_3$ (*trimethylcarbinol* or *methyl-2-propanol*), occurs in small proportion in fusel oil, and can be prepared by the action of hot 75 per cent. sulphuric acid on isobutylene, which thus takes up 1 mol. of water. When pure, it forms rhombic prisms or plates, m.pt. 25·5°, sp. gr. 0·786 (solid), b.pt. 83°. On oxidation it gives acetic acid, acetone, and carbon dioxide.

AMYL ALCOHOLS, $C_5H_{11} \cdot OH$. The eight isomerides theoretically possible are known, the most important being:

(1) Normal Amyl Alcohol, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OH$ (*pentanol*-1), b.pt. 138°, sp. gr. 0·817, is of little importance, and is obtained by reducing normal valeraldehyde or by the other general methods.

(2) Amyl Alcohol of Fermentation, $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH \cdot CH_2 \cdot CH_2 \cdot OH$ (*methyl-3-butanol*-1 or *isobutylcarbinol*), is a liquid, b.pt. 130°, sp. gr. 0·810, and is solid at −134°. It imparts its characteristic smell and burning taste to fusel oil, in which it abounds. It is to this alcohol that the poisoning effect of spirits is principally due. It occurs naturally in Roman chamomile oil.

(3) Active Amyl Alcohol, $\begin{matrix} C_2H_5 \\ CH_3 \end{matrix}\!\!>\!CH \cdot CH_2 \cdot OH$ (*methyl-2-butanol*-1 or *2-methylbutan-1-ol*), boils at 128°, has the sp. gr. 0·816, and is found with the amyl alcohol of fermentation. It contains an asymmetric carbon atom (*see* p. 19) and is lævo-rotatory, whilst the halogen compounds and the valeric acid derived from it are dextro-rotatory; also the dextro-isomeride of this acid yields a lævo-rotatory iodide.

(4) Tertiary Amyl Alcohol, $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C(OH) \cdot CH_2 \cdot CH_3$ (*methyl-2-butanol-2* or *amylene hydrate* or *dimethylethylcarbinol*) is an oily liquid with a faint odour of mint. It boils at 102° and is prepared from amylene by the indirect addition of water under the influence of sulphuric acid. It exerts a soporific action.

HIGHER ALCOHOLS. Of these may be mentioned: *Primary normal hexyl alcohol* or *hexanol*, $CH_3 \cdot [CH_2]_4 \cdot CH_2 \cdot OH$ (14 of the 18 hexyl alcohols predicted by theory are known), can be obtained from caproic acid, $C_6H_{12}O_2$, and is found as butyric and acetic esters in the ethereal oil of the seeds of *Heracleum giganteum* and in the fruit of *Heracleum spondylium*: it boils at 158° (under 740 mm. pressure), and has a specific gravity of 0·820. *Caproyl* or *isohexyl alcohol*, $(CH_3)_2 : CH \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OH$, b.pt. 150°, is found in vinasse and in fusel oil. *Heptyl* (or *œnanthyl*) *alcohol*, $C_7H_{16}O$; of the 38 possible isomerides, 13 are known. *Normal octyl alcohol*, $C_8H_{18}O$, is contained in *Heracleum spondylium* and *Heracleum giganteum*; *secondary octyl alcohol* (or *capryl alcohol* or *methylhexylcarbinol*) is formed on distilling castor oil. Other higher alcohols are obtained by reducing the corresponding aldehydes with zinc dust and acetic acid; they are almost solid, like paraffin wax. *Cetyl* or *normal hexadecyl alcohol*, $C_{16}H_{34}O$, combined with palmitic acid, forms the principal component of sperm oil. *Ceryl alcohol* (*cerotin*), $C_{26}H_{53} \cdot OH$, occurs as cerotic ester in Chinese wax and in wool-fat; it melts at 76° to 79°. *Melissyl* or *myricyl alcohol*, $C_{30}H_{61} \cdot OH$, is found as the palmitic ester in beeswax and carnauba wax and is obtained free by saponification with alcoholic potash.

II. UNSATURATED MONOHYDRIC ALCOHOLS

These are similar to the saturated alcohols, but, as they contain one or two double linkings, they behave like the olefines and diolefines in taking up two or four atoms of hydrogen, halogens, &c., to give saturated compounds. If they contain a triple linking, $-C \equiv CH$, they form explosive metallic compounds, as does acetylene (p. 91).

VINYL ALCOHOL, $CH_2 : CH \cdot OH$ (Ethenol), appears to be present in commercial ether, but it has never been isolated, attempts to synthesise it leading, as is the case with other similar compounds, to an isomeride—acetaldehyde, $CH_3 \cdot CHO$; the formation of the latter is explained by the addition of a molecule of water to the alcohol, and immediate loss of a molecule of water from the compound thus formed.

ALLYL ALCOHOL, $CH_2 : CH \cdot CH_2 \cdot OH$ (Propenol), is a liquid of pungent odour, b.pt. 97°, and readily soluble in water. It is formed in small quantity in the distillation of wood, but is more easily obtained by heating glycerol at 26° with oxalic acid and a little ammonium chloride. Cl, Br, CN, and HClO can be added on to it directly, but not H. When cautiously oxidised, it takes up O and H_2O, giving glycerol or even acrolein (allyl aldehyde) and acrylic acid, which shows it to be a primary alcohol.

CITRONELLOL, $C_{10}H_{20}O$, is found in attar of roses.

PROPARGYL ALCOHOL, $CH : C \cdot CH_2 \cdot OH$ (Propinol), is a liquid with a pleasant odour, lighter than water, b.pt. 114°.

GERANIOL, $C_{10}H_{18}O$ or $(CH_3)_2 : C : CH \cdot CH_2 \cdot CH_2 \cdot C(CH_3) : CH\, CH_2 \cdot OH$, is a pleasant-smelling oil, b.pt. 121° under 17 mm. pressure. It is obtained from geranium oil, and on oxidation gives *citral* (the corresponding aldehyde) which occurs in mandarin oil and in essences of orange and lemon and to a very considerable extent (60 per cent.) in verbena oil.

III. POLYHYDRIC ALCOHOLS

(a) DIHYDRIC ALCOHOLS OR GLYCOLS, $C_nH_{2n}(OH)_2$

Substitution of two hydrogen atoms joined to different carbon atoms by two hydroxyl groups gives dihydric alcohols, containing two alcoholic groups. It is not, however, possible to have two hydroxyl groups united to the same carbon atom—although similar compounds are known for the ether derivatives known as Acetals (*see later*)—since even if they could be formed they would immediately lose a molecule of water, forming aldehydes or ketones.

The dihydric alcohols, owing to their sweet taste, were called **Glycols** by Wurtz, who prepared them by transforming a dihalogenated hydrocarbon into the corresponding diacetyl-ester by means of silver acetate and then saponifying the diacetyl compound either by baryta or sodium hydroxide or by boiling with water and lead oxide or sodium carbonate solution:

$$\underset{\text{Ethylene bromide}}{\begin{array}{l} CH_2Br \\ | \\ CH_2Br \end{array}} + 2CH_3 \cdot COOAg = 2AgBr + \underset{\text{Diacetylglycol}}{\begin{array}{l} CH_2 \cdot O \cdot COCH_3 \\ | \\ CH_2 \cdot O \cdot COCH_3 \end{array}}$$

$$\begin{array}{l} CH_2 \cdot O \cdot COCH_3 \\ | \\ CH_2 \cdot O \cdot COCH_3 \end{array} + 2KOH = 2CH_3 \cdot COOK + \begin{array}{l} CH_2 \cdot OH \\ | \\ CH_2 \cdot OH \end{array} \text{(glycol)}$$

A special group of glycols, the *pinacones*, containing two adjacent tertiary alcohol groups ($\equiv C \cdot OH$), are formed by reducing the ketones with sodium and water, or, better, together with isopropyl alcohol, by electrolysing a dilute solution of sulphuric acid and acetone, the latter being reduced at the negative pole:

$$3CH_3 \cdot CO \cdot CH_3 + H_4 = CH_3 \cdot CH(OH) \cdot CH_3 + \begin{array}{l} CH_3 \cdot C(OH) \cdot CH_3 \\ | \\ CH_3 \cdot C(OH) \cdot CH_3 \end{array};$$

this *pinacone* (2 : 3-dimethyl-2 : 3-butandiol), melts at 38°, boils at 172° and crystallises with $6H_2O$. When distilled with dilute sulphuric acid, it is transformed into *pinacoline*, $(CH_3)_3C \cdot CO\ CH_3$, with separation of H_2O and transposition of an alkyl group.

The glycols have an almost oily appearance; their solubility and sweetness increase with the molecular weight; the specific gravity and boiling-point are much higher than those of the monohydric alcohols with equal numbers of carbon atoms. The hydroxyl groups of the glycols behave like those of monohydric alcohols, so that the glycols can give rise to ethers and esters, alkoxides (sodium, &c.), halogen compounds (*e.g.* the *chlorohydrins*), aldehydes and acids, besides which they may give up 1 mol. of H_2O forming anhydrides.

ETHYLENE GLYCOL (Ethan-1 : 2-diol), $C_2H_4(OH_2)$, is a dense liquid, b.pt. 198°, and, on oxidation, yields glycollic acid, $CO_2H \cdot CH_2 \cdot OH$ and oxalic acid, $CO_2H \cdot CO_2H$.

PROPYLENE GLYCOLS. Two isomerides are known: **α-Propylene Glycol**, $OH \cdot CH_2 \cdot CH(OH) \cdot CH_3$ (*propan-1 : 2-diol*), boils at 188° and is formed in the distillation of glycerol with sodium hydroxide. It contains an asymmetric carbon atom and, by the action of certain ferments, the lævo-rotatory isomeride can be isolated. **β-Propylene Glycol** boils at 216° and is formed by the bacterial decomposition of glycerol, as well as by the usual synthetical methods.

In the higher glycols, when the two hydroxyl groups have four carbon atoms between them (γ-glycols), water is readily separated and furan derivatives, analogous with pyrrole and thiophene compounds, formed.

(*b*) TRIHYDRIC ALCOHOLS, $C_nH_{2n-1}(OH)_3$

These are colourless, dense liquids with a sweetish taste and readily soluble in water; they contain at least three carbon atoms and three hydroxyl groups, and are hence capable of forming three series of esters by combination with a monobasic acid.

GLYCEROL, $C_3H_5(OH)_3$, or $OH \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot OH$ (Propantriol), was discovered by Scheele in 1779. Chevreul and Braconnot (1817) found it as a component of all oils and fats. Its formula and constitution were established later (Pelouze, Wurtz, and Berthelot). It occurs abundantly in nature, not in the free state, but combined with higher fatty acids in the form of esters (*glycerides*), which form the fats and oils; these contain 9 to 11 per cent. of combined glycerol.

It exists free in rancid fats and is formed in small proportions in the fermentation of sugar (all wines contain 0·98 to 1·67 per cent.). Industrially glycerol is obtained principally from factories where fats are decomposed (stearine- and soap-works). Synthetically it can be obtained by transforming propylene (from isopropyl iodide), by means of chlorine in the hot, into dichloropropane, $C_3H_6Cl_2$, which, with iodine chloride, gives the trichloro-derivative $C_3H_5Cl_3$; the latter, when heated with water at 170°, gives glycerol:

$$CH_2Cl \cdot CHCl \cdot CH_2Cl + 3H_2O = 3HCl + OH \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot OH.$$

This formation of glycerol and also that by the oxidation of allyl alcohol, $CH_2 : CH \cdot CH_2 \cdot OH$, demonstrate the constitution of glycerol. On the other hand, it is possible to prepare glycerol synthetically from the elements by way of acetylene, acetaldehyde (p. 91), acetic acid, acetone (by distillation of calcium acetate), isopropyl alcohol (by reduction), propylene, and thence, as above to glycerol (Friedel and Silva).

PROPERTIES. Glycerol (also termed glycerine) is an oily, colourless, dense (sp. gr. 1·265 at 15°) liquid, with a sweet taste; it is very hygroscopic and dissolves in all proportions in water and alcohol, heat being developed on mixing 58 parts of glycerol with 42 parts of water.

It is insoluble in ether and chloroform; it dissolves to the extent of 5 per

cent. in dry acetone and to a greater degree in aqueous acetone. It boils at 290° with partial decomposition, but it can be distilled unchanged in a vacuum (at 10 mm. pressure it boils at 162°). It crystallises at −40° or at a higher temperature if it contains water; the separated crystals melt only at 22°.

When heated for a long time at 130° to 160° in presence of sulphuric acid, glycerol loses one or more molecules of water, giving anhydrides or ethers of glycerol or *polyglycerines* (A. Nobel, 1890); W. Will (1904) arrived at the same result by heating glycerol for 7 to 9 hours at 290° to 295° and distilling off the water formed. This treatment yields about 60 per cent. of *diglycerol*, $C_3H_5(OH)_2 \cdot O \cdot C_3H_5(OH)_2$, and a little tri- and polyglycerols; all these products can be esterified like glycerol and yield, *e.g.* *tetranitrodiglycerine*, which does not congeal even at −20° and has an explosive power like trinitroglycerine (*see also* C. Claessen, Ger. Pats. 181,754 and 198,768, 1907). According to U.S. Pats. 978,443 (1910) and 13,234 (1911), glycerol readily polymerises when heated at 275° in presence of 0·5 to 1·0 per cent. of sodium acetate, 70 per cent. being polymerised in an hour.

When it is heated rapidly and strongly it decomposes, yielding partly acrolein with the characteristic pungent odour. Also when heated with P_2O_5 or $KHSO_4$, it loses $2H_2O$, giving acroleïn, $CH_2 : CH \cdot CHO$.

One hundred parts of glycerol dissolve the following quantities of mineral salts: 98 of sodium carbonate, 60 of borax, 50 of zinc chloride, 40 of potassium iodide, 10 of boric acid, 50 of tannin; bromine, ammonia, ferric chloride, &c., are also dissolved.

Glycerol has the refractive index 1·476 at 13° and in aqueous solution the index varies proportionally with the dilution. By means of Lenz's table, the concentration of glycerol solutions can be determined from either the specific gravity or the index of refraction:

Percentage of glycerol	Degrees Baumé, Beck, Gerlach	Sp. gr. at 12° to 14°	Index of refraction at 12·5° to 12·8°	Percentage of glycerol	Degrees Baumé, Beck, Gerlach	Sp. gr. at 12° to 14°	Index of refraction at 12 5° to 12·8°
98	30·1	1·2637	1·4729	48	16·2	1·1265	1·3979
96	29·6	1·2584	1·4700	46	15·5	1·1210	1·3950
94	29·1	1·2531	1·4671	44	15·0	1·1155	1·3921
92	28·7	1·2478	1·4642	42	14·3	1·1100	1·3890
90	28·2	1·2425	1·4613	40	13·6	1·1045	1·3860
88	27·7	1·2372	1·4584	38	13·0	1·0989	1·3829
86	27·1	1·2318	1·4555	36	12·3	1·0934	1·3798
84	26·6	1·2265	1·4525	34	11·5	1·0880	1·3772
82	26·1	1·2212	1·4496	32	11·0	1·0825	1·3745
80	25·6	1·2159	1·4467	30	10·3	1·0771	1·3719
78	25·1	1·2106	1·4438	28	9 6	1·0716	1·3692
76	24·5	1·2042	1·4409	26	9·0	1·0663	1·3666
74	24·0	1·1999	1·4380	24	8·3	1·0608	1·3639
72	23·5	1·1945	1·4352	22	7·6	1·0553	1·3612
70	23·0	1·1889	1·4321	20	6·9	1·0498	1·3585
68	22·3	1·1826	1·4286	18	6·1	1·0446	1·3559
66	21·6	1·1764	1·4249	16	5·6	1·0398	1·3533
64	21·0	1·1702	1·4213	14	4·9	1·0349	1·3507
62	20·3	1·1640	1·4176	12	3·8	1·0297	1·3480
60	19·8	1·1582	1·4140	10	3·4	1·0245	1 3454
58	19·2	1·1530	1·4114	8	2·8	1·0196	1·3430
56	18·6	1·1480	1·4091	6	2·1	1·0147	1·3405
54	18·0	1·1430	1·4065	4	1·3	1·0098	1·3380
52	17·4	1·1375	1·4036	2	0·7	1·0049	1·3355
50	16·9	1·1320	1·4007				

Glycerol has the interesting property of preventing the precipitation of various metallic hydroxides (*i.e.* it keeps them dissolved); for instance, in presence of glycerol, potassium hydroxide does not precipitate salts of chromium, copper, &c. With alkalis it forms slightly stable soluble alkoxides. It does not reduce silver or cupric salts, and hence cannot contain aldehyde groups; it is not coloured by concentrated sulphuric acid or by sodium hydroxide on boiling. The halogens act on glycerol, not as substituting, but as oxidising agents. It inverts cane-sugar and renders starch soluble; 100 parts of glycerol and six of starch at 190° give *starch soluble* in water, and the starch can be separated from the glycerol, when cold, by precipitation with alcohol.

Like the other polyhydric alcohols (glycols, erythritol, and its isomerides, also glucose and its isomerides—galactose, &c.—but not cane-sugar, quercitol or dextrin) glycerol, when added in sufficient quantity, transforms the alkaline reaction of borax solutions in an acid reaction, thus allowing of the determination of boric acid and borax by titration.

Under the action of certain schizomycetes, glycerol yields normal butyl alcohol, butyric acid and, partly, ethyl alcohol.

Being a trihydric alcohol, glycerol is able to form esters of three types (mono-, di- and tri-), according as one, two, or three hydroxyl groups are replaced by inorganic or organic acid residues. In this way the glycerides can be regenerated; for example, when excess of stearic acid is heated with glycerol at 200° under reduced pressure until no more water separates, *tristearin* is formed.

When cautiously oxidised, glycerol forms first *glyceric acid*, $OH \cdot CH_2 \cdot CH(OH) \cdot COOH$, which undergoes further oxidation to *tartronic acid*, $COOH \cdot CH(OH) \cdot COOH$, so that it is proved that glycerol contains two primary alcohol groups, $(\cdot CH_2 \cdot OH)$; also, as tartronic acid still exhibits alcoholic characters, it must contain a secondary alcohol group. The constitution of glycerol is hence completely proved.

USES OF GLYCEROL. The majority of the glycerol manufactured is used for the preparation of nitroglycerine and hence of dynamite (*see later*). It is also used to give body to light wines (termed *Scheelisation*, after Scheele, the discoverer of glycerol). It is employed in the manufacture of liqueurs, syrups, preserves, and sweetmeats, since it is sweet and dense, and, to some extent, anti-fermentative. It is added to chocolate, tobacco, cosmetics, textiles to be dressed, and leather goods, since it does not dry and keeps them soft or pliable. It is also used in extracting from flowers and herbs delicate perfumes which would undergo change if extracted by distillation.

It is employed as a non-congealing and lubricating liquid (a solution of sp. gr. 1·13) in gasmeters; for greasing iron objects to prevent them from rusting; for making copying-ink, soap, and shoe-polish; for preserving anatomical preparations, &c.

INDUSTRIAL PREPARATION. Glycerol is almost exclusively obtained as a secondary product in the treatment of fats. Until the year 1885 only the aqueous residues of stearine works were worked up (the fats are decomposed with lime, sulphuric acid, steam, or ferments), but nowadays almost all the alkaline lye of soap factories (where the fats are treated directly with caustic soda and then with salt) [1] are utilised.

Of the 9 to 11 per cent. of glycerol contained in fats, 8 to 10 per cent. can be recovered (only 4 per cent. when the decomposition is effected by sulphuric acid, the maximum yield being obtained when water or ferments are used).

The treatment of the dilute solutions of crude glycerol varies with their origin: soap-lyes (which are sometimes concentrated in the soap-works and sold to the glycerol refiners)

[1] These lyes have an alkaline reaction and, on analysis, one of them gave the following results: water, 61 per cent.; glycerol, 16.5 per cent. salts; 22 per cent. (eight-tenths of which were NaCl, one-tenth Na_2SO_4, and one-thirtieth Na_2CO_3). The specific gravity varies from 3° to 7° Bé., and the proportion of glycerol usually from 6 to 12 per cent.

are treated with 0·1 to 0·2 per cent. of lime or ferrous sulphate and mixed by means of an air-jet; the liquid is decanted, slightly acidified with hydrochloric acid and skimmed; a small quantity of aluminium sulphate is then added, the liquid being decanted, rendered slightly alkaline, passed through a filter-press and concentrated in open boilers furnished with stirrers until sodium chloride begins to separate; subsequent concentration to the sp. gr. 28° Bé. is carried out in a vacuum, the salt deposited being gradually removed. This crude *glycerol* contains 85 to 90 per cent. of glycerol and 1 per cent. of salts, and has a dark yellow or brownish colour. Sometimes the alkali is removed from the soap lyes by adding a little resin and boiling, so that the resin soap formed is carried to the surface and can be decanted (to be utilised by adding to ordinary soap).

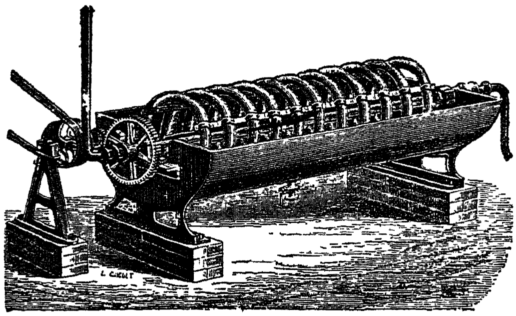


FIG. 172.

The free lime may also be precipitated with an oxalate or with carbon dioxide. The concentration is not carried out in open vessels, as, when the aqueous solutions are vigorously boiled, the steam given off carries away appreciable quantities of glycerol. The concentration is hence carried to a certain point in an apparatus (Fig. 172 shows the Droux apparatus and Fig. 173 that of Morane), fitted with rotating coils or hollow discs, in which steam under pressure circulates. The apparatus is covered in and the steam from the solution issues rapidly through a tube communicating with an aspirator. When the density reaches 18° to 20° Bé. the solution is decanted or filtered and then further concentrated in a vacuum to 27° to 28° Bé.

In some cases the glycerol thus obtained, while still boiling, is decolorised by adding animal charcoal and filtering through a filter-press. This glycerol always contains a small quantity of dissolved salts. To purify it, its temperature is raised to 110° to 120° by means of superheated steam, the acids or more volatile products being thus eliminated. It is then distilled with superheated steam at 170° to 180°, at which temperature all the pure glycerol passes over. This is rectified in one apparatus to 22° Bé. and in a second, under diminished pressure and with superheated steam, to 28° Bé., at which concentration almost all the salt separates. The vacuum distillation is sometimes effected by a triple-effect apparatus (Pick type, *see* vol. i, p. 453; *also* section on Sugar), with which it is easy to remove the salt as it separates without interrupting the distillation.

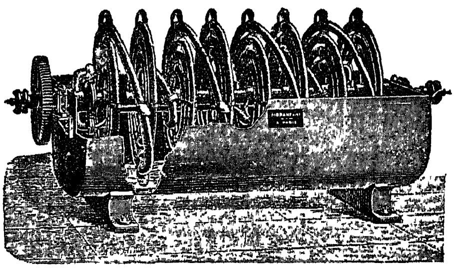


FIG. 173.

These forms of apparatus for purification and distillation are named after their inventors (Hagemann, Scott, Jobbins, van Ruymbeke, Lehmann, Heckmann, &c.).

The Heckmann process consists in distilling the aqueous glycerine, already concentrated to beyond 20° Bé., in a boiler, *A* (Fig. 174), into which steam superheated to 200° to 220° and under half an atmosphere pressure is passed by means of a perforated coil. In order to prevent the scum being carried over with the steam and glycerol, a perforated disc, *a*, fitted with a vent-pipe is fixed two-thirds of the way up the boiler. The vapours issue by the pipe *B*, and are condensed in the reservoir, *C*, which is heated to 80° to 90° with indirect steam circulating in the jacketed bottom, *D*. Above the reservoir is a rectifying column, with a dephlegmator, *K*, similar to, but much lower than, that used for the rectification of alcohol (*see* p. 136).

During the distillation, a slight vacuum is maintained in the whole apparatus by means of a suction pump, *V*, so that principally water-vapour and only a little glycerol are evolved from the reservoir, *C*. The glycerol vapour separates in the column and returns to the reservoir, whilst the condenser, *M*, condenses only the water-vapour, which is controlled

by its density, colour, and taste in the test-glass, *N*, and is then collected in the tank, *O*. In *C* the glycerol finally reaches a concentration of 95 to 99 per cent.

The rectifying column is sometimes replaced by a series of communicating, vertical copper tubes (Fig. 175) which fractionally condense the glycerol- and water-vapours from the boiler, *B* (heated partly by direct fire), into which passes steam from *v*, superheated

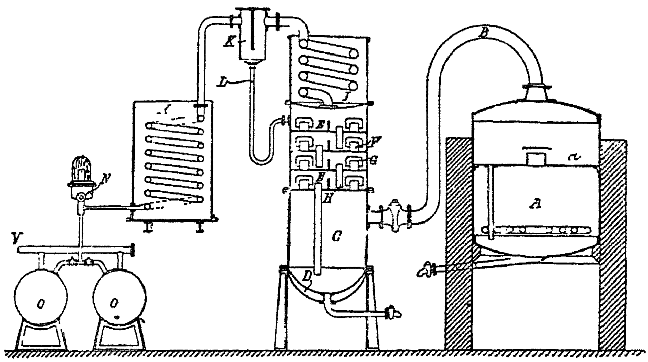


Fig. 174.

in the furnace, *T*. By means of the pump, *Z*, a vacuum is maintained in the whole apparatus, so that, as the distillation proceeds, fresh glycerine from the reservoir, *A*, can be drawn into the boiler. In the first cylinder or condensing tube, which soon reaches a temperature of 100°, almost pure glycerol separates, whilst in the succeeding tubes, cooled only by the surrounding air, more and more dilute glycerine and finally water separate. Below each tube is a horizontal cylinder, these serving to collect the glycerols of different concentrations, some of which are subjected to redistillation. In this way is obtained the best *dynamite glycerine*, which must have a specific gravity of 1·263 (98 to 99 per cent.), and should not contain lime, sulphuric acid, chlorine, or arsenic.

The final decoloration may also be effected by sodium hydrosulphite. Very pure

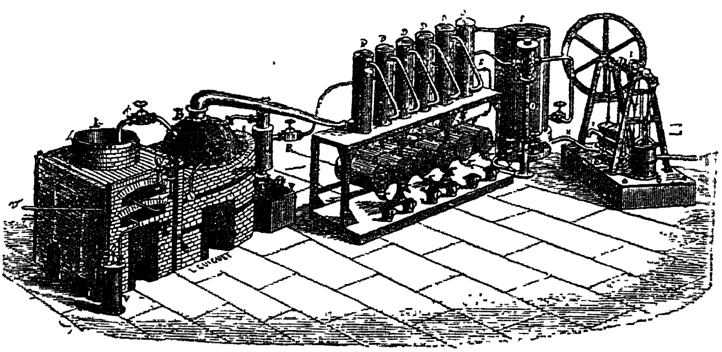


Fig. 175.

glycerol has been obtained by maintaining it at 0° for some time and then inducing crystallisation by a few pure crystals obtained separately by cooling to − 40° (Kraut's process). The degree of purity is increased by a second crystallisation.

Purification by an osmotic process has also been attempted but with unsatisfactory results.

During the last few years the glycerine liquids from the biological or catalytic decomposition of fats (*see* section on Fats) have also been worked up: they are first neutralised or, better, rendered slightly alkaline with milk of lime and, after being left for some time, the liquid is decanted or filtered off, concentrated to 15° Bé. *in vacuo*, again allowed to stand to deposit a further quantity of lime, decolorised by passing through a carbon filter and again concentrated to 28° Bé.

Various attempts have also been made to recover the glycerine from the waste liquors from the manufacture of alcohol, but as yet without much success (Ger. Pats. 114,492,

125,788, 129,578, 141,703, and 147,558). Separation of glycerine by dialysis does not give good results.

STATISTICS AND PRICES. In 1890, the world's production of crude glycerine amounted to 26,000 tons from candle factories and 14,000 tons from soap factories, the amounts due to the principal nations being: France, 6000 tons (candles), 3500 tons (soap); Germany, 3000 and 2000; England, 1200 and 5500; Italy, 180, &c.

In 1900 the production rose to 80,000 tons (equally divided between soap and candle factories) and Germany, with a production of about 10,000 tons, exported 2730 tons (value about £140,000) in 1900 and 1580 tons in 1909, against importations of 5373 tons in 1908 and 3530 tons in 1909. In 1890 France exported 3856 tons (value £156,000), in 1900 about 7450 tons (value £308,000), and in 1909 as much as 7000 tons out of a total production of 12,000 tons; 9000 tons were made at Marseilles, where the most important refinery produces more than 2000 tons per annum. The French exportation is now directed especially to the United States (more than 4000 tons in 1910). According to the official statistics (!) Italy produced 190 tons of distilled glycerine (worth £8660) in 1905 and 215 tons (value £12,040) in 1908; the imports were 198 tons in 1907 and 1908, 160 tons in 1909 and 270 tons in 1910; and the exports 833 tons in 1908, 1145 tons (worth £59,540) in 1909, and 1763 tons (value £126,920) in 1910.

In 1910 Spain produced 2500 tons of glycerine and exported 893 tons. In 1905 the United States produced 23,000 tons (£1,040,000), of which 13,500 tons were obtained from soap-works; the imports amounted to 16,000 tons in 1909 and to more than 20,000 tons in 1910. England exported 10,500 tons (one-half in the crude state) in 1909 and about 12,500 tons (£1,040,000) in 1910; in 1911 the output was 16,000 tons, one-half of which was refined.

Two main qualities of glycerine are distinguished:[1] (*a*) *Crude glycerine* from the candle or soap works; (*b*) *Refined glycerine*, which is subdivided into: pale, white, for dynamite, and chemically pure.

In 1905–1909 the price of No. II dark brown crude glycerine at 24° Bé. was 30*s*. 6*d*. per quintal, and at 28° Bé. 36*s*. per quintal; for the light brown quality, 46*s*. 6*d*. per quintal at 28° Bé., and for the pale at 28° Bé. £4. Yellow refined at 28° Bé. cost 93*s*.; white refined No. I, 96*s*. at 28° Bé. and 108*s*. at 30° Bé.; free from lime for soap, £5 at 28° and 108*s*. at 30° Bé. Finally the purest double distilled glycerine for nitroglycerine at 31° Bé. cost £6 per quintal. At the beginning of 1910 these prices were increased by 25 per cent. and towards the end of 1910 by 50 per cent. or even 70 per cent. At the beginning of 1911 they were still higher mainly owing to the large amount required in North America for making dynamite for the Panama Canal and other public works.

C. TETRA- AND POLY-HYDRIC ALCOHOLS

These are usually sweet, crystalline substances which decompose near their boiling-points. They are distinguished one from another by the crystalline forms of their phenylhydrazine derivatives.

[1] Tests for Glycerine: the *crude*, pale at 28° Bé., contains 0·5 per cent. of ash and is not rendered turbid by HCl, and only faintly so by lead acetate; that separated from sulphuric acid saponifications, besides having a bad smell and taste, gives 3 to 5 per cent. of ash and 84 to 86 per cent. of glycerine, a turbidity (fatty acids) or precipitate being produced by HCl or lead acetate. The glycerine to be used for nitroglycerine and dynamite is subjected to the following tests: the *water* is calculated from the loss in weight of 20 grms. heated for 10 hours at 100° and for a few hours at a slightly higher temperature. Five grammes, after being heated in a platinum dish at 180° until no further evolution of vapour takes place, are weighed, and should then undergo no further diminution in weight when again heated for a short time; it is then ashed in the usual way and the ash tested for metals and salts. *Glycerine for nitroglycerine* should have been distilled at least once, should not contain sugar or fatty acids, should have a neutral reaction and should contain no lead, calcium, or other metals or foreign metalloids; only traces of Cl, As, and Fe are allowed: the specific gravity should exceed 1·262. The purest glycerine (puriss.) does not contain more than 0·03 per cent. of ash and as much organic impurity, and for dynamite these two should not exceed 0·25 per cent. Oxalic acid is detected by neutralising with ammonia, acidifying with acetic acid and precipitating with $CaCl_2$. The glycerine content is determined from the density (the air-bubbles being removed by heating), use being made of the Table on p. 184; in Germany a special Berthelot scale is used indicating one degree higher than the Baumé scale, 26° Berthelot corresponding with a specific gravity of 1·210, 28° with 1·230, 29° with 1·240, and 30° with 1·250. The index of refraction is determined at the temperature indicated in the Table. In many cases the glycerine is estimated directly by means of the *acetyl number* (*see* succeeding Note), but the method in which the glycerine is oxidised by hot permanganate and potassium hydroxide to oxalic acid and the latter precipitated as calcium oxalate should be rejected. The fairly rapid Hehner-Richardson-Jaffe method is used more successfully: the glycerine is destroyed with dichromate and sulphuric acid, and the amount of dichromate used up (or, according to Gautter and Schulze, how much CO_2 is evolved) measured by titration with sodium thiosulphate, or, better, ferrous ammonium sulphate. This method assumes that the glycerine contains no chloride, nitrate, or extraneous organic matter; these impurities can, in any case, be eliminated by means of silver oxide (chlorides), and lead acetate and calcium carbonate (organic matter), decoloration being then effected by heating with animal charcoal.

They do not reduce Fehling's solution and hence differ from the carbohydrates, but are derived from these by reduction.

The *valency of an alcohol* is given by the number of alcoholic hydroxyls it contains, and hence by the number of monobasic acid residues it can fix to form a neutral ester. Acetic anhydride serves well for this purpose, the hydrogen atoms of the hydroxyl groups being replaced each by an acetyl group, $CH_3 \cdot CO$:[1]

$$\underset{\text{Mannitol}}{C_6H_8(OH)_6} + 6(CH_3 \cdot CO)_2O = 6CH_3 \cdot COOH + \underset{\text{Hexacetylmannitol}}{C_6H_8(O \cdot CO \cdot CH_3)_6}.$$

Esters can also be prepared with bromobenzoic acid, the bromine in the resultant product being determined and the number of hydroxyl groups deduced therefrom. Well-defined compounds are also formed with benzaldehyde and are employed in separating the constituents of different mixtures.

ERYTHRITOL (Butantetrol), $OH \cdot CH_2 \cdot CH(OH) \cdot CH(OH) \cdot CH_2 \cdot OH$, is found in nature in the free state in *Protococcus vulgaris*, and as orsellinic ester (erythrin) in lichens and algæ. It forms crystals, m.pt. 112°, b.pt. 330°, and is slightly soluble in alcohol and insoluble in ether. It is obtained by decomposing *d*-glucose or synthetically from crotonylene, and its constitution is deduced from the fact that it yields secondary normal butyl iodide on reduction with hydriodic acid. A similar reaction takes place with the higher polyvalent alcohols with normal chains. The four possible stereoisomerides are known, the most common being the one now described which is optically inactive.

PENTA-ERYTHRITOL has the formula $C(CH_2 \cdot OH)_4$, and melts at 253°.

ARABITOL, $C_5H_7(OH)_5$ (Pentahydroxypentane), crystallises in acicular prisms, m.pt. 102°, has a sweet taste and is formed by reducing the corresponding sugar, arabinose, with nascent hydrogen ; reduction of xylose similarly yields xylitol.

MANNITOL, $C_6H_8(OH)_6$ (Hexanhexol), occurs abundantly in the vegetable kingdom (the larch, sugar-cane, *Agaricus integer* containing 20 per cent. of mannitol, &c.), but especially in the manna ash (*Fraxinus ornus*), the dried juice of which forms ordinary *manna;*[2]

[1] In this way is determined the so-called *acetyl number* which is so widely used in the analysis of fats and oils. With these, the test is made on the insoluble *fatty acids* obtained by saponifying 40 to 50 grms. of the fat with 40 c.c. of KOH solution (sp. gr 1 4) and 40 c c. of alcohol, this mixture being heated for half an hour on the water-bath, after which it is diluted with a litre of water and boiled for three-quarters of an hour in an open beaker to eliminate the alcohol. The liquid is acidified with sulphuric acid and boiled until the fatty acids separate in a transparent condition, when they are removed with a tapped funnel, washed twice with hot water and dried in an oven at 100° to 105°. To determine the acetyl number, a few grammes of the substance containing the hydroxyl groups (or about 20 grms. of hydroxylic fatty acids) are treated with two or three times their volume of acetic anhydride and a few drops of concentrated sulphuric acid (formerly in place of the sulphuric acid fused sodium acetate, in quantity equal to the acetic anhydride, was used, the mixture being heated for two hours on the water-bath in a reflux apparatus). The mass heats spontaneously, and in a few minutes acetylation takes place ; it is then allowed to cool, calcium carbonate being added to precipitate the sulphuric acid and the liquid filtered The filtrate is distilled or evaporated to separate the acetate in a liquid or crystalline condition.

In the case of the fatty acids, the filtrate is, however, diluted with 600 to 700 c c. of water and boiled for 30 to 40 minutes in an open beaker to remove the acetic acid, a slow current of CO_2 being passed into the bottom of the liquid to prevent bumping. The supernatant liquid is then siphoned from the acetyl compound, which is boiled with another 500 c.c. of water and so on, this operation being repeated until the washing water no longer has an acid reaction. The acetylated derivative is then collected on a filter, washed and dried in an oven.

Of this compound, 0·5 to 1 grm. is dissolved in pure, neutral alcohol, and the solution heated for 45 minutes on the water-bath in a 150 c c. flask with a definite volume (30 to 50 c c.) of seminormal alcoholic potash. When cold, the liquid is titrated with seminormal hydrochloric acid in presence of phenolphthalein to determine the excess of alkali which has not taken part in the splitting of the acetic ester.

One hydroxyl group for every grm -mol. of substance corresponds with 56 grms of KOH fixed. With the fatty acids, which contain also the carboxyl group, the procedure is as follows : 3 to 4 grms of the acetyl derivative are dissolved in pure, neutral alcohol and the acidity of the carboxyl group (*acetyl acid value*) determined by titration with N/2-alkali ; the neutralised liquid is boiled with a known volume in excess of N/2-alcoholic potash for a short time on the water-bath, retitration with N/2-hydrochloric acid given the excess of alkali not combined with acetyl groups. The alkali combined (after the first neutralisation), expressed in mgrms. of KOH per 1 grm. of acetyl compound gives the *acetyl number*. With the fatty acids the sum of the acetylated acid number and the acetyl number is termed the *acetyl saponification value*. From the acetyl number (N), the molecular magnitude (M), of the alcoholic substance can be deduced by the formula : $M = \frac{56{,}100}{N} - 42$.

[2] Manna is extracted more particularly from *Fraxinus ornus* and *Fraxinus rotundifolia*, which are widespread in Sicily and Calabria and from which it readily flows through long vertical incisions made in summer and autumn. It seems to occur in the rising sap before this reaches the leaves and is thought by some to be produced by enzyme actions. Crude, commercial manna contains 12 to 13 per cent. of water, 10 to 15 per cent. of sugar, 32 to 42 per cent. of mannitol, 40 to 41 per cent. of mucilaginous substances, organic acids and nitrogenous matter, 1 to 2 per cent. of insoluble substances and 1 to 2 per cent. of ash *Australian manna* (from *Myoporum platycorpum*) contains as much as 90 per cent. of mannitol.

The manna tree grows in fertile, rocky soil and is incised in its tenth year and in the following 10 or 15 years. It

from this alcohol extracts pure mannitol, which can be decolorised by repeated treatment with charcoal. In manna it was discovered by Proust in 1806. It is obtained synthetically by reducing fructose or glucose: $C_6H_{12}O_6 + H_2 = C_6H_{14}O_6$.

The optically inactive, lævo- and dextro-rotatory forms are known, the last being the most common; the optical activity is slight but is rendered more apparent by the addition of borax. When heated it loses water giving anhydrides (*mannitan*, $C_6H_{12}O_5$, and *mannide*, $C_6H_{10}O_4$); in a vacuum it distils unchanged.

One hundred parts of water dissolve 16 parts by weight of mannitol at 16°.

From alcohol it crystallises in triclinic acicular prisms and from water in large rhombic prisms having a sweet taste and melting at 160°.

Stereoisomeric with mannitol is DULCITOL, $C_6H_8(OH)_6$, which occurs in a number of plants and in Madagascar manna. It forms sweet, monoclinic prisms, m.pt. 188°, and is almost insoluble in water, even in the hot. Synthetically it can be prepared by reducing lactose and galactose. It is optically inactive even in presence of borax.

Another stereoisomeride of mannitol is sorbitol, which melts at 104° to 109°, or at 75° when crystallised with $1H_2O$. It can be obtained synthetically by reducing *d*-glucose or *d*-fructose. In presence of borax it shows a slight dextro-rotation.

Other stereoisomerides are TALITOL and IDITOL; these isomerides are usually separated by means of the acetals they form with benzaldehyde.

DD. DERIVATIVES OF THE ALCOHOLS

A. DERIVATIVES OF MONOHYDRIC ALCOHOLS

I. ETHERS

These are generally formed by eliminating 1 mol. of water (for example, by concentrated sulphuric acid or by hot hydrochloric acid) from 2 mols. of alcohol, which condense to form 1 mol. of ether in the same way as 2 mols. of an acid give an anhydride:

$$\begin{matrix} C_2H_5\cdot OH \\ CH_3\cdot OH \end{matrix} = H_2O + \begin{matrix} C_2H_5 \\ CH_3 \end{matrix}\Big\rangle O.$$

Ethers are not formed by secondary or tertiary alcohols. The first term of the series, methyl ether, is gaseous, and the succeeding terms become liquid and then solid as the molecular weight increases, the ethereal odour of the first members being gradually lost.

is then cut back and the new branches incised in the seventh year and the succeeding 10 or 15 years. It is then again cut back, this procedure being continued for 80 or 100 years. One hectare with 4500 trees gives as much as 100 kilos of manna per annum. It is harvested in August and September.

Manna is used as a mild purgative for children. It has a sweetish taste, is soluble in water or alcohol, and, besides mannitol, contains various sugars such as *stachyose* and *mannatriose*.

To extract the mannitol, the crude manna is dissolved in half its weight of water containing white of egg. The solution is boiled for a few minutes and strained, and the filtered mass, solidified by cooling, pressed in bags, or, better, centrifuged and washed at the same time with a large quantity of cold water. It is redissolved in water and the solution boiled with animal charcoal, filtered under pressure, crystallised and centrifuged. The mother-liquors are used to dissolve fresh quantities of the crude manna. The fineness of the crystals depends on the concentration and on the temperature of the air; in some cases the crystallisation is disturbed by continually stirring the mass.

Sometimes the manna solutions are first subjected to lactic fermentation, by which means considerable quantitie of calcium lactate are obtained; the mannitol is then extracted from the residual liquors.

Mannitol is not fermented by beer-yeast, but with chalk and sour cheese it gives a considerable amount of alcohol, volatile acids, carbon dioxide, and hydrogen. When cautiously oxidised with nitric acid, it forms *d*-mannose and *d*-fructose, whilst with the *Sorbose bacterium* it gives only the latter sugar.

Mannitol has a slight lævo-rotation (− 0·15°) which is increased by alkali and changed in sign by borax. It dissolves in 6 5 parts of water at 18°, in 80 parts of 60 per cent. alcohol at 15°, or in 1400 parts of absolute alcohol; it is insoluble in ether.

Manna in casks costs 3*s*. to 5*s*. per kilo; assorted, 1*s*. 7*d*.; in lumps, 9½*d*. The average price of manna (from Cefalu) on the Genoa Exchange has gradually risen from about 2*s*. 1*d*. in 1901 to about 4*s*. 7*d*. in 1910, when pure crystallised mannitol cost 7*s*. to 10*s*. per kilo. The best qualities of manna are those from Cefalu, Gerace, and Smauro; of inferior quality is the Capaci variety, which is produced also at Cinisi, Belmonte, Castellamare del Golfo, &c. The Sicilian production, which represents almost the entire production of the world, was about 3600 quintals in 1900, 7000 in 1902, 5100 in 1905, 6900 in 1906, 4550 in 1908, and less than 3000 (owing to the bad season) in 1910. The exports were 2320 quintals in 1907, 1776 in 1908, 2582 (value £36,000) in 1909. About 3000 quintals per annum are treated for the extraction of mannitol—about 1000 quintals, of which only one-third or one-fourth is consumed in Italy.

The empirical formulæ of the ethers show them to be isomeric with the alcohols, but their constitution results from Williamson's synthesis, according to which they are obtained by the action of a sodium alkoxide on the halogen derivative of an alcohol:

$$C_mH_{2m+1}ONa + IC_nH_{2n+1} = NaI + C_mH_{2m+1} \cdot O \cdot C_nH_{2n+1}$$

If in the sodium alkoxide the sodium were not united to the oxygen but directly with carbon, this reaction would give an alcohol and not an ether; indeed, if sodium ethoxide were $NaCH_2 \cdot CH_2 \cdot OH$, it would, with methyl iodide, give propyl alcohol: $CH_3I + NaCH_2 \cdot CH_2 \cdot OH = NaI + CH_3 \cdot CH_2 \cdot CH_2 \cdot OH$. But, in reality, methyl ethyl ether and not propyl alcohol is obtained, this proving the constitution of the metallic alkoxides and of the ethers, in which all the hydrogen atoms are equivalent.

The interaction of silver oxide with alkyl halides (*see* p. 17) also leads to the formation of ethers: $2C_2H_5I + Ag_2O = 2AgI + C_2H_5 \cdot O \cdot C_2H_5$.

If the alkyl radicles of an ether are similar, it is a *simple ether*, *e.g.* ethyl ether, $C_2H_5 \cdot O \cdot C_2H_5$, whereas if the radicles are different, the result is a *mixed ether*, *e.g.* methyl ethyl ether, $C_2H_5 \cdot O \cdot CH_3$.

Sabatier, Senderens, and Mailhe (1909–1910) obtained ethers of different types, some mixed and of the aromatic series, by passing the superheated vapours of alcohols (250° to 350°) over metallic oxides (titanium, thorium, tungsten, or, best of all, aluminium). The yield is quantitative, no ethylene hydrocarbons being formed as is the case when sulphuric acid is used. The process is continuous and pseudo-catalytic, unstable aluminium alkoxide being formed as an intermediate product: $(C_2H_5O)_6Al_2 = Al_2O_3 + 3(C_2H_5)_2O$. In some cases this general method can be advantageously employed industrially.

When the ethers are prepared from the alkoxides in alcoholic solution there should not be an excess of water (more than 50 per cent.) present, otherwise the alkoxide decomposes into alcohol and alkali hydroxide and no ether is formed.

Also when sulphuric acid (or HCl) is used in the preparation, an equilibrium sets in between the reacting products—intermediate and final—this equilibrium being regulated by the mass law, so that a certain yield cannot be exceeded except by eliminating some of the new products formed (*e.g.* by gradually distilling the ether; *see later*):

$$(a)\ C_2H_5 \cdot OH + H_2SO_4 = \underset{\text{Ethylsulphuric acid.}}{C_2H_5 \cdot SO_4H} + H_2O.$$

$$(b)\ C_2H_5 \cdot SO_4H + C_2H_5 \cdot OH = H_2SO_4 + C_2H_5 \cdot O \cdot C_2H_5.$$

The sulphuric acid is regenerated and can transform fresh alcohol into ether; theoretically, then, the initial quantity of sulphuric acid should be sufficient to transform an infinite quantity of alcohol into ether, but in practice it is necessary to add a small quantity of the acid each time, as some of it is used up in the formation of sulphur dioxide, ethylene, and sulphonated products. The process is thus not practically continuous in the strict sense of the term, since in the phase (*a*) water is formed, and this cannot all be eliminated by distillation, but after a time accumulates in such quantity as to establish an equilibrium between the formation of ether and the decomposition of ethylsulphuric acid, alcohol and sulphuric acid thus being regenerated.

The ethers are very stable and scarcely react in the cold with alkalis, dilute acids, sodium or phosphorus pentachloride. When superheated with water and a little mineral acid, ether is converted back into alcohol:

$$C_2H_5 \cdot O \cdot C_2H_5 + H_2SO_4 = C_2H_5 \cdot OH + C_2H_5 \cdot SO_4H$$

and the same change occurs on saturating ether at 0° with gaseous hydrogen iodide:

$$(C_2H_5)_2O + HI = C_2H_5 \cdot OH + C_2H_5I,$$

the hydrogen iodide subsequently converting the alcohol also into ethyl iodide;

when mixed ethers are taken, the iodine unites preferably with the radicle containing the lesser amount of carbon. PCl_5 also decomposes the ethers on heating:

$$(C_2H_5)_2O + PCl_5 = POCl_3 + 2C_2H_5Cl.$$

The halogens give substitution products just as they do with the hydrocarbons, but nitric acid gives oxidation products.

In the ethers are reproduced all the cases of isomerism presented by the alkyl groups from which they are derived, there being consequently numerous cases of *metamerism* (*see* p. 17), *e.g.* methyl amyl ether, $CH_3 \cdot O \cdot C_5H_{11}$, is metameric with ethyl butyl ether, $C_2H_5 \cdot O \cdot C_4H_9$, and also with dipropyl ether, $C_3H_7 \cdot O \cdot C_3H_7$, all these having the empirical formula $C_6H_{14}O$.

METHYL ETHER, $CH_3 \cdot O \cdot CH_3$ (Methoxymethane), is a gas, but liquefies at −23°, and then has a sp. gr. 1·617; it resembles ethyl ether. One volume of water dissolves 37 vols. of the gas, and 1 vol. of sulphuric acid 600 vols. of it.

ETHYL ETHER, $C_4H_{10}O$ (Ethoxyethane), $C_2H_5 \cdot O \cdot C_2H_5$. This was prepared for the first time in the sixteenth century by Valerius Cordus from spirit of wine. It was formerly thought to contain sulphur, and was therefore given the name *sulphuric ether*, still in use. Its true composition was established by Saussure and by Gay-Lussac (1807 and 1815) and the constitution was enunciated by Laurent and Gerhardt and confirmed experimentally by Williamson. It was thought for a long time that the sulphuric acid employed in the manufacture of ether possessed the sole function of fixing and subtracting water from the alcohol. Since, however, it was found that water formed in the reaction always distilled with the ether, this hypothesis became invalid, and Berzelius and Mitscherlich attributed the reaction of etherification to the catalytic action of the sulphuric acid.

Later on Liebig maintained that the ether is formed by the direct decomposition of the intermediate product (ethylsulphuric acid) with separation, in the hot, of SO_3. Graham, however, succeeded in showing that ethylsulphuric acid, when heated alone at 140°, does not give ether, but that the latter is formed in presence of alcohol. In 1851 Williamson gave the true explanation of the process by dividing the reaction into two phases (*a* and *b*, *see* preceding page); the secondary products, explaining the loss of sulphuric acid (*see above*), were discovered later.

Etherification takes place also if the sulphuric acid is replaced by phosphoric, arsenic, boric, or hydrochloric acid.

Sulphur dioxide, which is formed and lost in this process, is not produced if the sulphuric acid is replaced by an aromatic sulphonic acid, for instance, $C_6H_5 \cdot SO_3H$, or the corresponding chloride, $C_6H_5 \cdot SO_2Cl$ (Kraft and Ross, Ger. Pat. 691,115), the temperature of the reaction being then slightly above 100°:

$$(a)\ C_2H_5 \cdot OH + C_6H_5 \cdot SO_3H = H_2O + C_6H_5 \cdot SO_2 \cdot OC_2H_5.$$

$$(b)\ C_2H_5 \cdot OH + C_6H_5 \cdot SO_2 \cdot OC_2H_5 = (C_2H_5)_2O + C_6H_5 \cdot SO_3H.$$

J. W. Harris's process (U.S. Pat. 711,656) may also have an industrial future; in this, acetylene and hydrogen give ethylene which, with H_2SO_4, forms ethylsulphuric acid, the latter then forming ether under the action of water.

Good results are also given by the use of *methionic acid*, $CH_2(SO_3H)_2$, proposed by Schroeter and Sondag in 1908; with this acid all the higher ethers can be prepared and 10 per cent. of the acid (on the weight of alcohol) is sufficient to give a continuous distillation of ether.

Senderens transforms alcohol vapour quantitatively into ether by passing it over calcined, precipitated alumina heated exactly to 260° (*see* p. 191).

PROPERTIES. Ether is a colourless, very mobile liquid boiling at 34·9°, solidifying at −129°, and melting at −113°; it has the sp. gr. 0·7196 at 15°. At 120° its vapour pressure is 10 atmos. On evaporation, it produces intense cold. It inflames very readily, but is not inflammable when mixed with 35 to 50 per cent. of carbon tetrachloride. With air it forms explosive mixtures (p. 33). It is obtained anhydrous by distilling over a little sodium.

J. Meunier (1907) has found that mixtures of ether vapour and air become inflammable and explosive when they contain from 75 to 200 mgrms. of ether per litre of air.

As ether vapour is much heavier than air (mol. wt. 74), it tends to collect in a dense, invisible layer on the floor or bench and may cause fire or explosion. It is soluble in concentrated hydrochloric acid.

Water dissolves 6·5 per cent. of ether at 19°, and ether dissolves about 1·25 per cent. of water at 20°. Aqueous ether can be recognised by the turbidity produced on shaking it with a small quantity of carbon disulphide. It is moderately soluble in concentrated sulphuric acid (1 vol H_2SO_4 dissolves 1·67 vol. of ether). It is an excellent solvent for many organic substances. It combines with certain inorganic substances (chloride of tin, aluminium, phosphorus, antimony, &c.) as ether of crystallisation.

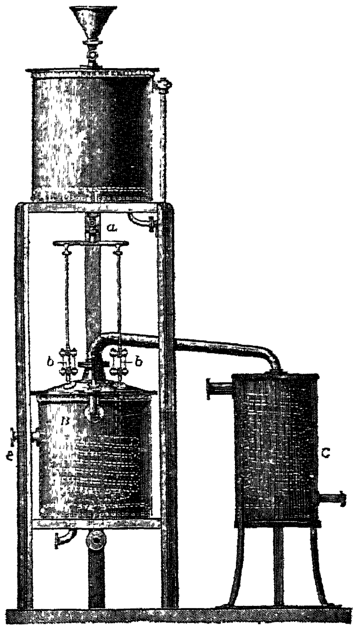


FIG. 176.

The action of light on ether produces small quantities of hydrogen peroxide, acetaldehyde, acetic acid, and vinyl alcohol. In contact with platinum black, ether ignites. When poured into a cylinder of chlorine it explodes and forms hydrogen chloride, whilst in the dark the slow reaction yields perchloroether. Ether is an *anæsthetic* and was used as such before chloroform; it is again coming into use at the present time, as it is not very dangerous, although it produces certain disturbing effects, for example, in the lungs. For this purpose it must be used in a highly purified condition.

When mixed with liquid carbon dioxide, it lowers the temperature to 79·5° below zero. It decomposes at above 500°, giving acetaldehyde.

INDUSTRIAL PREPARATION OF ETHER. Use is generally made of the continuous process, the apparatus employed being that of Boullay or of Barbet; 9 parts of concentrated sulphuric acid of 66° Bé. (free from nitric and nitrosylsulphuric acids, which would attack the copper of the apparatus) and 5 parts of 90 per cent. alcohol free from fusel oil are taken. Heckmann's apparatus for working on a small scale is shown in Fig. 176: *A* is the alcohol reservoir which feeds the alcohol regularly through the tap, *a*, and the glass vessel, *b*, to the still, *B*, containing the sulphuric acid; indirect steam under pressure is supplied to the coil, *e*. The ether continually distilling over is condensed in the coil, *C*, immersed in cold water.

The Barbet apparatus (Fig. 177) is used for the production of large quantities of ether, and consists of a vertical cylindrical boiler, *A*, inside which is the steam coil, *C*. The alcohol is introduced by the central tube, *H*, whilst another tube is used at the beginning for the acid and still another, of greater width, allows the ether vapour to escape to the saturator and the condenser. The boiler and the coils are of copper or of iron lined with lead.

First of all, 3500 kilos of sulphuric acid (66° Bé.) and 1500 kilos of 95 per cent. alcohol are introduced and are heated to 130° by means of the steam-coil; as the ether

distils alcohol is automatically added in a continuous stream. To remove the acid products carried over by the ether, use is made of a *saturator* (Fig. 178), which contains a number of plates like a rectifying column and down which flows a solution of soda.

The crude ether, distilled and condensed in the refrigerating coil, contains a little alcohol, water, and other impurities; to dry and purify it, it is redistilled over calcium chloride and then rectified in a column apparatus. Distillation over sodium wire yields a very pure product.

The premises where the distilling apparatus is situated are usually separated by thick walls from the condenser, in order to avoid the danger of fire and explosion. Some premises are fitted with channels and draught-apertures for rapidly dispersing any vapour which may find its way into the air. The distilled vapour is condensed in closed apparatus, the only outlet to which is a tube opening on the roof.

If the temperature of etherification exceeds 140°, the yield diminishes, as a considerable quantity of ethylene is then formed: $C_2H_5 \cdot OH = H_2O + C_2H_4$. On the other hand, if the temperature falls below 130°, a large amount of alcohol distils without reacting.

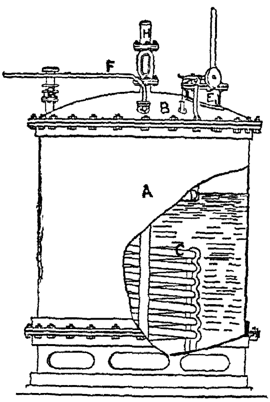


Fig. 177.

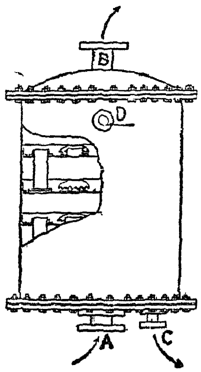


Fig. 178.

The alcohol for making ether is denatured so as to be exempt from taxation, and in Germany animal oil (Dippel's) is added, this being then fixed and decomposed by the sulphuric acid. In Italy the alcohol is denatured with sulphuric acid.

D. Annaratone (Ger. Pat. 231,395, 1909) obtains increased yields of ether by passing alcohol vapour, superheated to 130°, into a column filled with pebbles, among which the sulphuric acid is circulated or sprayed; for 100 kilos of ether only 180 kilos of steam are required for heating instead of 700 kilos used in the old process.

USES AND PRODUCTION. The amount of ether manufactured in Germany in 1902 was about 2000 tons, without counting that now made in large quantities for the production of artificial silk by the Chardonnet-Lehner process.

In Italy large amounts of ether were manufactured before the artificial silk factories were closed; it is protected by a Customs duty of £3 12*s*. The importation into Italy has fallen to 25 quintals. In 1907, Gulinelli's distillery (Ferrara) alone produced 3588 quintals of ether. Owing to the crisis in the Italian artificial silk industry, the production had fallen considerably in 1910.

Ether exempt from duty is sold in Germany at £4 per quintal if its sp. gr. is 0·722, whilst the price of the pharmacopœial product, sp. gr. 0·720, is £4 10*s*. Taxed ether, distilled over sodium and chemically pure, costs 4*s*. per kilo. In 1909, ether for artificial silk manufacture cost £2 11*s*. per quintal in Belgium and £2 14*s*. in Austria.

Ether is used in small quantity as an anæsthetic, and in large quantities in the manufacture of collodion and artificial silk, and also as a solvent for numerous organic compounds in dye and perfume factories. In Ireland it is drunk as a liqueur—a refined form of alcoholism.

Various chlorinated derivatives of ether are known.

Also **Ethyl Peroxide, $C_2H_5 \cdot O \cdot O \cdot C_2H_5$**, is prepared by introducing ethyl groups into hydrogen peroxide by means of ethyl sulphate; it is a liquid, b.pt. 65°, soluble in water and very readily inflammable, but is moderately stable towards chemical reagents.

In 1901 Baeyer prepared also the **Hydrate of Ethyl Peroxide, $C_2H_5O \cdot OH$**, as a colourless

liquid, which possesses strong oxidising properties, dissolves in water, boils at 95°, and forms barium and other salts.

TESTS FOR ETHER. Ether containing water or alcohol has a specific gravity of 0·720–0·722–0·725 or even 0·733. When 20 c.c. of ether are shaken with 5 c.c. of water, the latter should not exhibit an *acid* reaction. The presence of ozone or hydrogen peroxide in ether is revealed by potassium iodide solution, which turns brown within an hour in the dark. If water is present, the ether imparts a green or blue colour to ignited white copper sulphate.

In a mixture of alcohol and ether, Fleischer and Frank (1907) determine the proportions of the two components by pouring 10 c.c. into a graduated cylinder containing 5 c.c. of benzene and 5 c.c. of water. After shaking, the increase in volume of the water gives the alcohol and the increase in volume of the benzene shows the quantity of ether.

II. THIO-ALOCOHLS AND THIO-ETHERS

These have the same constitution as the alcohols and ethers, excepting that the oxygen is replaced by sulphur. They are very volatile and inflammable liquids, almost insoluble in water and having repulsive garlic-like odours; in the higher members, however, the odour diminishes and the solubility in water vanishes, although they continue to be soluble in alcohol or ether.

(*a*) THIO-ALCOHOLS (or Mercaptans or Thiols or Alkyl Sulphydrates), $C_nH_{2n+1}SH$, have lower boiling-points than the corresponding alcohols. They are feebly acid in character and form salts called Mercaptides, *e.g.* with mercuric oxide. They are soluble in concentrated alkali solutions. They may be regarded as hydrogen sulphide in which one atom of hydrogen is replaced by an alkyl radicle, *e.g.* ethanthiol or ordinary Mercaptan, C_2H_5SH. As acids they are monobasic, and salts are formed with metallic sodium or potassium; the lead salts are yellow and are obtained by the action of lead acetate in alcoholic solution. Nitric acid transforms the mercaptans into *alkylsulphonic acids:* $C_2H_5SH + 3O = C_2H_5 \cdot SO_3H$.

With iodine, the salts of sodium, &c., give *disulphides:*

$$2C_2H_5SNa + I_2 = 2NaI + (C_2H_5)_2S_2,$$

which, with hydrogen, give mercaptans, and with nitric acid *disulphoxides*, $(C_2H_5)_2S_2O_2$; concentrated sulphuric acid gives disulphides and is itself reduced to sulphur dioxide.

(*b*) THIO-ETHERS (or Alkyl Sulphides), $(C_nH_{2n+1})_2S$, are neutral, readily volatile liquids, and afford a good illustration of the variability of the valency of sulphur (di- to hexa-valent).

They may be regarded as derived from hydrogen sulphide by replacement of the two hydrogen atoms by alkyl groups. With salts they form double *compounds*, *e.g.* ethyl sulphide with mercuric chloride gives $(C_2H_5)_2S, HgCl_2$. They combine with halogens, giving, for instance, $(C_2H_5)_2SBr_2$, whilst when treated with dilute nitric acid they fix an atom of oxygen, yielding, *e.g.* $(C_2H_5)_2SO$, ethyl sulphoxide; with more energetic oxidising agents, a further oxygen atom is taken up with formation of *sulphones*, *e.g.* Diethylsulphone, $(C_2H_5)_2SO_2$. With hydrogen, the sulphoxides give sulphides, but the sulphides are not reduced. They combine with alkyl haloids, forming *sulphonium* compounds, *e.g.* ethyl iodide and ethyl sulphide give Triethylsulphonium Iodide, $(C_2H_5)_3SI$, which reacts like metallic iodides with silver hydroxide, yielding Triethylsulphonium Hydroxide, $(C_2H_5)_3S \cdot OH$.

METHODS OF FORMATION. They are obtained: (1) by heating alkyl haloids or salts of alkylsulphuric acid with an alcoholic or aqueous solution of potassium sulphide or hydrosulphide: $C_2H_5Br + KSH = KBr + C_2H_5SH$: $2C_2H_5Br + K_2S = 2KBr + (C_2H_5)_2S$; $2C_2H_5 \cdot SO_4K + K_2S = 2K_2SO_4 + (C_2H_5)_2S$.

(2) By the action of phosphorus pentasulphide, P_2S_5, on ethers. *Mixed sulphides* can also be obtained by these and various other methods.

METHYL HYDROSULPHIDE (Methanthiol), $CH_3 \cdot SH$, is found among the gases from the anaerobic decomposition of proteins (for instance, in the intestines of animals). It is a nauseous liquid, lighter than water and boiling at 6°.

METHYL SULPHIDE, $(CH_3)_2S$, is a liquid, b.pt. 37°, having a disagreeable ethereal odour.

ETHYL HYDROSULPHIDE (Ethanthiol, Ethylmercaptan, or Mercaptan), $C_2H_5 \cdot SH$, is a liquid, b.pt. 36°, having a repulsive odour and is used for the preparation of *sulphonal*. With sodium ethoxide in alcoholic solution it gives **Sodium Mercaptide**, C_2H_5SNa, in white crystals; **Mercuric Mercaptide**, $(C_2H_5S)_2Hg$, has also been obtained.

ETHYL SULPHIDE, $(C_2H_5)_2S$, is a liquid, b.pt. 92°, insoluble in water, and forms a crystalline bromide $(C_2H_5)_2SBr_2$.

ETHYL DISULPHIDE (Ethanodithioethane), $(C_2H_5)_2S_2$, boils at 151°, and is obtained by the action of iodine on mercaptan.

ETHYL SULPHOXIDE (Ethanosulphoxyethane), $(C_2H_5)_2SO$, is a dense liquid, soluble in water, and readily reducible.

ETHYLSULPHONE (Ethanosulphonethane, Diethylsulphone), $(C_2H_5)_2SO_2$, boils unchanged and does not undergo reduction.

TRIMETHYLSULPHONIUM IODIDE, $(CH_3)_3SI$, obtained from sulphur and methyl iodide, forms white crystals soluble in water and with silver hydroxide gives the **Hydroxide** $(CH_3)_3SOH$, which is an energetic base and displaces ammonia from its salts.

III. ETHERS OF ALCOHOLS WITH INORGANIC ACIDS

Ethers formed from an alcohol residue and an acid residue are termed **Compound Ethers or Esters.** We shall here describe those derived from mineral acids and shall consider organic acid esters more in detail when the acids themselves have been studied. The esters may be regarded as derived either from acids by the replacement of the acid hydrogen by an alkyl residue, as with the salts, or from alcohols by replacing the hydroxylic hydrogen by an acid radicle:

$$HNO_3 \quad . \; . \; . \quad KNO_3 \quad . \; . \; . \quad C_2H_5 \cdot NO_3$$

$$\text{or} \quad C_2H_5 \cdot OH \quad . \; . \; . \quad C_2H_5 \cdot O(NO_2) \quad . \; . \; . \quad C_2H_5 \cdot O(SO_3H).$$

Monobasic acids form only one class of esters, viz. *normal esters*.

Dibasic acids form two series of esters, *normal* and *acid*: *e.g.* $C_2H_5HSO_4$, acid esters, and $(C_2H_5)_2SO_4$, normal ester.

Tribasic acids give three kinds of esters with constitutions analogous to those of the salts.

The **Normal Esters** are neutral liquids of agreeable odour, moderately volatile and insoluble in water.

The **Acid Esters** have acid reactions, are less stable, odourless, soluble in water, and volatile without decomposition.

In general, these esters are decomposed by alkali or water at a high temperature (150° to 180°), the components being regenerated; this change is known as *Saponification*: $C_2H_5NO_3 + KOH = C_2H_5 \cdot OH + KNO_3$.

FORMATION. (1) They are usually formed by the interaction of the components (absolute alcohol + acid), the water which gradually forms being fixed and the resulting ester distilled. With some acids, the corresponding salts in presence of concentrated sulphuric acid at 100° to 130° are taken, so that the acid is obtained in the nascent state and the ester driven off as it is formed. They are more readily obtainable by saturating the mixture of alcohol and salt with gaseous hydrogen chloride.

(2) From the silver salt of the acid and alkyl iodide:

$$Ag_2SO_4 + 2C_2H_5I = 2AgI + SO_4(C_2H_5)_2.$$

(3) From the alcohol or alkoxide with the chloride of the acid :

$$SOCl_2 + 2C_2H_5OH = 2HCl + SO(OC_2H_5)_2 \text{; and}$$

$$POCl_3 + 3C_2H_5ONa = 3NaCl + PO(OC_2H_5)_3 \textit{ (ethyl phosphate)}.$$

(4) By passing the vapours of the acid and alcohol together over a catalyst as much as 50 per cent. of the ester is obtained.

1. ESTERS OF SULPHURIC ACID AND ALKYLSULPHURIC ACIDS. These are generally prepared from fuming sulphuric acid and alcohol, or from silver sulphate and alkyl iodide or from alcohol and sulphuryl chloride,

$$SO_2Cl_2 + 2C_2H_5OH = 2HCl + SO_2(C_2H_5O)_2 \text{;}$$

acid esters (*alkylsulphuric acids*) also exist. Tertiary alcohols do not form these esters.

Ethyl Sulphate, $(C_2H_5)_2SO_4$, is an oily liquid with an odour of mint and a pronounced acid character ; it boils at 208° and is easily saponified, even by boiling with water alone. It is formed by heating ethylsulphuric acid :

$$2C_2H_5SO_4H = SO_4H_2 + SO_4(C_2H_5)_2.$$

Ethylsulphuric Acid, $C_2H_5SO_4H = (C_2H_5O{\cdot}SO_3H)$, is formed as an initial product in the manufacture of ether (p. 192). It is soluble in water and is distinguished from sulphuric acid by the solubility of its calcium, strontium, barium, and lead salts. It gives well crystallised salts, the potassium salt being largely used for preparing ethyl derivatives, *e.g.* when it is dry-distilled with potassium bromide :

$$KBr + C_2H_5SO_4K = SO_4K_2 + C_2H_5Br.$$

2. DERIVATIVES OF SULPHUROUS ACID : (a) Sulphurous Esters ; (b) Sulphonic Acids.

(*a*) **Ethyl Sulphite,** $SO_3(C_2H_5)_2$, and ethylsulphurous acid, $C_2H_5SO_3H$. The latter is known also in the form of salts and both are readily saponified, since the sulphur is not directly united with carbon : $CH_3{\cdot}CH_2{\cdot}O{\cdot}SO_2H$.

(*b*) **Ethylsulphonic Acid,** $C_2H_5{\cdot}SO_3H$, is obtained by the reaction

$$C_2H_5I + SO_3Na_2 = NaI + C_2H_5SO_3Na \text{;}$$

or by oxidising the thioalcohols : $C_2H_5SH + O_3 = C_2H_5{\cdot}SO_3H$; or thus :

$$2C_2H_5I + Ag_2SO_3 = 2AgI + (C_2H_5)_2SO_3 \textit{ (ethyl ethylsulphonate)}.$$

Sulphonic acid compounds are not saponifiable ; diethylsulphonic acid is saponifiable to the extent of one-half, since in the sulphonic acids the sulphur is united with carbon : $CH_3{\cdot}CH_2{\cdot}SO_2{\cdot}OH$; the presence of hydroxyl is shown by the fact that with PCl_5 it forms $C_2H_5{\cdot}SO_2Cl$, which with hydrogen gives *ethylsulphinic acid,* $C_2H_5SHO_2$, the salts of the latter reacting with alkyl haloids to form *sulphones.*

3. ESTERS OF NITRIC ACID. These are explosive if heated rapidly and undergo saponification when boiled with an alkali. Tin and hydrochloric acid *reduce them,* giving **Hydroxylamine,** NH_2OH, the nitrogen being separated from the radicle as in saponification.

Ethyl Nitrate : $C_2H_5O{\cdot}NO_2$, is a liquid boiling at 86°.

4. ESTERS OF NITROUS ACID. These are easily obtained by passing nitrogen trioxide (N_2O_3) into the alcohols, or by treating the latter with alkali nitrites and sulphuric acid. They are reduced by nascent hydrogen, giving alcohol and ammonia.

Ethyl Nitrite, $C_2H_5O{\cdot}NO$, was at one time called *nitric ether.* Dissolved in alcohol, it bears the name *spiritus ætheris nitrosi,* and is used to modify the taste of various substances. It is also used for preparing diazo-compounds.

5. NITRO-DERIVATIVES OF THE HYDROCARBONS. These are *isomeric with nitrous esters* but they boil at higher temperatures than the latter and are distinguished from them by being non-saponifiable and by giving organic amino-compounds on reduction, as long as the nitrogen is not severed from the organic radical :

$$CH_3{\cdot}NO_2 \text{ (nitromethane)} + 3H_2 = 2H_2O + CH_3{\cdot}NH_2.$$

They are formed by treating alkyl iodides with silver nitrite :

$$CH_3I + AgNO_2 = AgI + CH_3{\cdot}NO_2 \text{;}$$

with the higher members of the series, the nitrous esters are formed at the same time

and may be separated by distillation. Of the various methods of formation, mention may be made of that based on the action of *dilute* nitric acid, in the hot and under pressure, on the paraffins :

$$\underset{\text{Hexane}}{C_6H_{14}} + HNO_3 = \underset{\text{Nitrohexane}}{C_6H_{13}\cdot NO_2} + H_2O.$$

Concentrated nitric acid does not give nitro-compounds with the paraffins, but with aromatic hydrocarbons it reacts readily.

The difference in *constitution* between *nitro-derivatives, e.g.* $H_3C\cdot NO_2$, and nitrous esters, *e.g.* $H_3C\cdot O\cdot N : O$, explains their different relations as regards saponification.

This also confirms the hypothetical constitution of nitrous acid, $O : N\cdot OH$. The hydrogen of the carbon atom united to nitrogen can be partially substituted by metals or bromine, since it has acquired acid characters—for instance, $NaCH_2\cdot NO_2$—but the acidifying influence of the nitro-group is not extended to the hydrogens of the other carbon atoms.

These nitroparaffins react with nitrous acid differently according as they are primary, secondary, or tertiary :

(*a*) **Nitroethane,** $CH_3 - C\begin{matrix}\diagup H_2 \\ \diagdown NO_2\end{matrix} + NO_2H = H_2O + CH_3 - C\begin{matrix}\diagup N\cdot OH \\ \diagdown NO_2\end{matrix}$ *i.e.* ethylnitric acid, salts of which are red.

(*b*) **Secondary Nitropropane,** $\begin{matrix}CH_3 \diagdown \\ CH_3 \diagup\end{matrix} C \begin{matrix}\diagup H \\ \diagdown NO_2\end{matrix} + NO_2H = H_2O + \begin{matrix}CH_3 \diagdown \\ CH_3 \diagup\end{matrix} C \begin{matrix}\diagup N = O \\ \diagdown NO_2\end{matrix}$,

propylpseudonitrole, which forms *blue* salts.

(*c*) Tertiary derivatives give no reaction.

These reactions serve well to distinguish *primary, secondary,* and *tertiary alcohols.*

Nitroethane may be used in the manufacture of explosives to lower the freezing-point of nitroglycerine.

CHLOROPICRIN, $CCl_3\cdot NO_2$, boils at 112°, and is formed by the simultaneous action of nitric acid and chlorine on various organic compounds.

NITROFORM, $CH(NO_2)_3$, and **TETRANITROMETHANE,** $C(NO_2)_4$, are crystallisable substances which boil unchanged. R. Schenck (Ger. Pat. 211,198, 1908) has prepared tetranitromethane in various ways.

6. Various esters of *hyponitrous, phosphoric, boric, silicic,* &c., acids are known.

DERIVATIVES OF HYDROCYANIC ACID

A. NITRILES. B. ISONITRILES

These compounds are formed by the substitution of the hydrogen of hydrocyanic acid by an alkyl radical, but they are not true esters, as they do not give the acid and alcohol again on hydrolysis.

A. NITRILES (or **Alkyl Cyanides**), are either liquid or solid, and have a pleasant, faintly garlic-like, ethereal odour. They are lighter than water, in which the first terms are soluble without undergoing change. They boil at about the same temperatures as the corresponding alcohols.

PREPARATION. 1. They are obtained by distilling a potassium alkylsulphate with potassium cyanide or with anhydrous potassium ferrocyanide, or by heating the cyanide at 180° with methyl iodide :

$$CH_3I + KCN = KI + CH_3\cdot CN \text{ (\textit{methyl cyanide} or \textit{acetonitrile}).}$$

2. Distillation of ammonium salts of *monobasic* acids yields amido-compounds which, with a dehydrating agent (P_2O_5, P_2S_5 or PCl_5), give nitriles :

$$(a)\ \underset{\text{Acetic acid}}{CH_3\cdot COOH} + NH_3 = H_2O + \underset{\text{Acetamide}}{CH_3\cdot CO\cdot NH_2};$$

$$(b)\ CH_5CO\cdot NH_2 - H_2O = \underset{\text{Acetonitrile or Methyl cyanide}}{CH_3\cdot CN.}$$

3. The higher nitriles are formed from the acid-amides containing one more carbon atom or from the primary amine containing the same number of carbon atoms, by treatment with sodium hydroxide and bromine ; or from the aldehydes which, with hydrocyanic acid, give the *nitriles of higher acids*, the so-called *cyanohydrins* or *hydroxynitriles*, liquid compounds easily saponified with regeneration of the aldehyde :

$$\underset{\text{Acetaldehyde}}{CH_3\cdot C\begin{matrix}\nearrow O \\ \searrow H\end{matrix}} + HCN = \underset{\text{Ethylidenecyanohydrin}}{CH_3\cdot CH\begin{matrix}\nearrow OH \\ \searrow CN\end{matrix}}.$$

PROPERTIES. When boiled with alkali or acid, or treated with superheated steam, nitriles give ammonia and an acid, from which products they can also be formed :

$$(a)\ CH_3CN + H_2O = CH_3\cdot CO\cdot NH_2\ (\textit{acetamide})\ ;$$
$$(b)\ CH_3\cdot CO\cdot NH_2 + H_2O = CH_3\cdot CO\cdot OH + NH_3.$$

This reaction is of importance for the synthesis of organic acids since, starting from a given alcohol and transforming it into iodide and then nitrile, an acid of the saturated series containing an extra carbon atom is obtained.

If the cyanide is treated with hydrogen sulphide instead of water, *thioacetamide*, $CH_3\cdot CS\cdot NH_2$, is obtained. With hydrochloric acid, the nitriles form *chloramides* or *chlorimides*, whilst with ammoniacal bases they give *amidines* (*see later*). Nascent hydrogen converts them into *amines* : $CH_3\cdot CN + 2H_2 = CH_3\cdot CH_2\cdot NH_2$ (*ethylamine*). By potassium or gaseous hydrogen chloride the nitriles are polymerised.

ACETONITRILE (or Methyl Cyanide), $CH_3\cdot CN$, is found among the products of distillation of beetroot molasses and of tar. It is soluble in water and boils at 82°.

B. ISONITRILES (Isocyanides or Carbylamines) are colourless liquids which have a faint alkaline reaction and boil at rather lower temperatures than the corresponding nitriles. They are insoluble in water but dissolve in alcohol or ether. They have repellent odours and are poisonous. They are obtained by the interaction of alkyl iodides with silver cyanide (whilst with potassium cyanide the nitriles are obtained) :

$$C_2H_5I + AgCN = AgI + C_2H_5\cdot NC\ ;$$

they are also formed by treating the primary amines with chloroform and alcoholic potash (*see* p. 100 ; *also later* under Amines).

Although they are stable towards alkalis, the isonitriles are readily decomposed by water giving formic acid and the corresponding amino-base containing one carbon atom less than the isonitrile :

$$CH_3\cdot NC + 2H_2O = H\cdot COOH + CH_3\cdot NH_2.$$

From the nitriles they are distinguished also by the different additive compounds which they form with halogens, hydrogen chloride, hydrogen sulphide, &c. At high temperature certain isonitriles change into nitriles.

CONSTITUTION OF THE NITRILES AND ISONITRILES. The nitriles have the carbon atom of the cyanogen group attached to the alkyl radicle and when they are hydrolysed only the nitrogen is removed as ammonia. Acetonitrile would hence have the constitution, $CH_3 - C\equiv N$.

The isonitriles, on the other hand, readily form amino-bases with loss of an atom of carbon—that of the cyanogen group—the nitrogen remaining with the radicle. Methylisocyanide or methylcarbylamine would hence have the formula $CH_3 - N\equiv C$.

IV. NITROGENATED BASIC ALKYL COMPOUNDS (AMINES)

If one or more of the hydrogen atoms of the ammonia molecule is replaced by one or more alkyl radicles, substances called Amines are formed; these have a basic character, which is in some cases more marked than that of ammonia itself (in the dissociation of compounds of the ammonia type, free anions, OH', are formed). To ammonia they present other chemical analogies. They have disagreeable ammoniacal odours; with mineral acids they form white, crystalline, deliquescent salts which are extremely soluble in water and have a basic nature, the nitrogen then becoming pentavalent; for the first members of the series the electrical conductivity is very high, higher indeed than that of ammonia, since N/100 solutions are almost completely dissociated.

Like ammonia, they give, with platinum chloride, crystalline platinichlorides, *e.g.* methylamine platinichloride, $(NH_2 \cdot CH_3, HCl)_2PtCl_4$; they also form double salts with gold chloride, $NH_2 \cdot C_2H_5$, HCl, $AuCl_3$. They precipitate heavy metals from solutions of their salts, and, in excess, sometimes redissolve them. The first terms are gases, after which come unpleasant smelling liquids soluble in water. The higher members are odourless and insoluble in, and lighter than, water; they are soluble in alcohol and in ether.

The ammonia derivatives are deliquescent solids, and in their behaviour greatly resemble potassium hydroxide, &c. According as they contain one or more alkyl radicals, these bases are called *primary* or *aminic*, *secondary* or *iminic*, *tertiary* or *nitrilic*, *quaternary* or *ammoniacal*.

PROCESSES OF FORMATION. (*a*) By heating an alkyl halogen compound with ammonia:

(1) $NH_3 + C_nH_{2+1}I = HI + C_nH_{2n+1}NH_2$; the halogen hydracid formed unites with the ammonia and with the amine, converting these partly into the corresponding salts; distillation with potassium hydroxide then gives: $KI + H_2O +$ the free base, $C_nH_{2n+1} \cdot NH_2$. The latter, which is partly free before treatment with potash, can in its turn react with a second molecule of the alkyl halogen compound, giving a secondary amine;

(2) $C_nH_{2n+1} \cdot NH_2 + C_nH_{2n+1}I = (C_nH_{2n+1})_2NH, HI$; the free base, which can be liberated by distilling with KOH, reacts with a third molecule of the alkyl halogen compound, yielding a tertiary amine;

(3) $(C_nH_{2n+1})_2NH + C_nH_{2n+1}I = (C_nH_{2n+1})_3N, HI$. Finally, the tertiary base, which remains free or can be liberated, reacts with a fourth molecule of the halogen derivative, giving the salt of the quaternary base;

(4) $(C_nH_{2n+1})_3N + C_nH_{2n+1}I = (C_nH_{2n+1})_4NI$, which is no longer a crystalline ammonia base and is not decomposed by potassium hydroxide, being more energetic than the latter; the hydrogen iodide formed unites with the amines if such are still present. When heated, the iodide of the quaternary base is converted back into the tertiary base and alkyl iodide, whilst with silver hydroxide it gives the corresponding solid alkylammonium hydroxide. In this general reaction, the four bases are always formed together, although more of one or another is obtained according to the nature of the alkyl group, the temperature, the duration of the reaction, and the quantity of ammonia present.

The separation of the bases in this mixture is not easy, and when these are present as salts, distillation with potassium hydroxide yields the primary, secondary, and tertiary amines, whilst the quaternary ammonium compound remains unchanged. The three bases or the corresponding salts are separated partly by crystallisation or by fractional distillation, or, better, by means of *ethyl oxalate*, $C_2O_2(C_2H_5O)_2$, which gives solid or liquid oxamides [*e.g. solid dimethyloxamide*, $C_2O_2(NH \cdot CH_3)_2$ and the ethyl ester of *dimethyloxaminic acid*, $C_2H_2(OC_2H_5) \cdot N(CH_3)_2$].

Amines can also be prepared by the following reactions:

(*b*) By the action of potassium hydroxide on alkyl isocyanates, *e.g.* *ethyl isocyanate*, $C_2H_5NCO + 2KOH = K_2CO_3 + C_2H_5 \cdot NH_2$;

(*c*) By reducing nitro-compounds, nitrites, oximes, or hydrazones with nascent hydrogen.

PROPERTIES. The amines do not undergo hydrolysis and are resistant to the action of acids, alkalis, and, to some extent, oxidising agents. The hydrogen combined with the nitrogen of amines can be replaced not only by alkyl groups (*see above*), but also by acid radicals (*e.g.* by *acetyl*, $CH_3 \cdot CO \cdot$) and mixed amines with alkyl and acidic groups can also be obtained. A characteristic and sensitive reaction of the *primary amines* is that with chloroform in presence of alkali, which gives rise to the unpleasant-smelling isonitriles: $CHCl_3 + CH_3 \cdot NH_2 + 3KOH = CH_3 \cdot NC + 3KCl + 3H_2O$. In alcoholic solution the primary and secondary bases form, with carbon disulphide, derivatives of thiocarbaminic acid, and only when these are derived from the primary bases can isothiocyanates be obtained. It is easier to distinguish (and separate) primary, secondary, and tertiary amines by their reactions with nitrous acid. When a hydrochloric acid solution of the mixture is treated with a concentrated solution of sodium nitrite, the primary amine yields the corresponding alcohol (soluble in water), with evolution of nitrogen:

$$C_nH_{2n+1}NH_2 + NOOH = H_2O + N_2 + C_nH_{2n+1}OH.$$

The secondary amines give oily *nitrosamines*, almost insoluble in water: $(C_nH_{2n+1})_2NH + NOOH = H_2O + (C_nH_{2n+1})_2N \cdot NO$; with feeble reducing agents, the nitrosamine is transformed into a *hydrazine*, whilst with more energetic reducing agents or with concentrated hydrochloric acid the secondary amine is regenerated, showing that the nitrous residue NO is joined to the iminic nitrogen and not to the carbon. The tertiary amine does not react with nitrous acid and is hence left unchanged in the solution, from which it can be obtained by distillation in presence of caustic soda.

Finally, the three classes of amines can be distinguished by the quantities of methyl iodide with which they react to produce the final quaternary base (*see preceding page*), with generation of greater or less quantities of ionisable compounds (titratable HI).

METHYLAMINE, $CH_3 \cdot NH_2$, is found ready formed in certain plants, *e.g.* in the dog-mercury weed (*Mercurialis perennis*). It is formed in the distillation of wood and occurs in beetroot and bone residues and in herring brine. It is a gas like ammonia and precipitates various metallic salts, but, when added in excess, does not dissolve nickel and cobalt hydroxides; it is more highly basic and more soluble in water than ammonia, and has a strong odour of ammonia and rotten fish. It becomes liquid at $-6°$ and at $-11°$ has the sp. gr. 0·699. With sodium hydroxide and bromine it gives acetamide. Its *hydrochloride*, $CH_3 \cdot NH_2,HCl$, is a crystalline, deliquescent substance extremely soluble in alcohol. With aluminium sulphate its sulphate forms an alum containing $24H_2O$.

DIMETHYLAMINE, $(CH_3)NH$, is a liquid boiling at $+7°$, and is formed, together with acetic acid, in the distillation of wood.

TRIMETHYLAMINE, $(CH_3)_3N$, is a gas which liquefies at $+3°$, and has an intense odour of rotten fish. It is found in various plants (*Arnica montana*, shoots of the pear-tree, &c.), and in herring brine. It is formed by the decomposition of betaïne during the distillation of beetroot molasses (p. 96).

ETHYLAMINE, $C_2H_5 \cdot NH_2$, is a liquid, b.pt. $+19°$, and smells strongly of ammonia, which it surpasses in basicity. It dissolves very readily in water with generation of heat. It dissolves aluminium hydroxide, and to a small extent cupric hydroxide but not ferric or cadmium hydroxide.

DIETHYLAMINE, $(C_2H_5)_2NH$, is a liquid, b.pt. 56°, and does not dissolve zinc hydroxide.

TRIETHYLAMINE, $(C_2H_5)_3N$, is an oily liquid which precipitates metals from their salts but does not redissolve the precipitates. It has a strongly alkaline reaction and boils at 89°. It is extremely soluble in cold water, but above 20° it becomes completely insoluble, separating from the water in an oily layer.

A group of nitrogen compounds which may be considered as formed by the condensation of ammonia (*hydrazine, azoimide, hydroxylamine,* &c.) has been already mentioned in vol. i, pp. 327 and 332. The alkyl derivatives of hydroxylamine, $NH_2 \cdot OH$, are divided into two groups: *α-alkylhydroxylamines*, in which the alkyl replaces the hydroxylic hydrogen $NH_2 \cdot OR$, and which hence have an ether character and do not reduce Fehling's solution; and *β-alkylhydroxylamines*, in which the alkyl radical replaces an amino-hydrogen and is therefore joined to the nitrogen, R—NH—OH; these reduce Fehling's solution even in the cold and on energetic reduction yield primary amines.

Also the **Alkylhydrazines**, $RNH—NH_2$, $R_2N \cdot NH_2$, &c., unlike amines, reduce Fehling's solution in the cold and give characteristic reactions with aldehydes and ketones.

The **Diazo-compounds** of the methane series are of slight importance, whilst those of the aromatic series are a very important class of compounds; the former differ from the latter in that the characteristic divalent nitrogen group, —N=N—, has its valencies saturated by *only one* carbon atom. **Diazomethane**, CH_2N_2, which is a yellow, poisonous gas, is prepared from hydroxylamine and dichloromethylamine.

V. PHOSPHINES, ARSINES, AND ALKYL METALLIC COMPOUNDS

Like ammonia, the hydrogen derivatives of phosphorus, arsenic, antimony, &c., give rise to alkyl compounds which have a very feebly basic character and a very unpleasant odour.

1. **PHOSPHINES.** These are gases or colourless liquids with repulsive odours. Their basic properties and their stability towards water become more marked as the number of alkyl groups increases. They are readily oxidisable with nitric acid, the remaining hydrogen atoms of the PH_3 being transformed into hydroxyl groups. The quaternary phosphonium bases are very strongly basic, and, unlike the corresponding ammonium bases, they lose an alkyl group in the form of a saturated hydrocarbon when heated, the residue being a *trialkylphosphonium oxide.*

$C_nH_{2n+1}PH_2$	$(C_nH_{2n+1})_2PH$	$(C_nH_{2n+1})_3P$	$(C_nH_{2n+1})_4P \cdot OH$
Primary phosphine	Secondary phosphine	Tertiary phosphine	Tetralkylphosphonium hydroxide

$C_nH_{2n+1}PO(OH)_2$	$(C_nH_{2n+1})_2PO \cdot OH$	$(C_nH_{2n+1})_3PO$
Alkylphosphonic acid	Dialkylphosphonic acid	Trialkylphosphine oxide

The primary and secondary phosphines are formed by heating phosphonium iodide with alkyl iodides and zinc oxide, whilst the tertiary phosphines and phosphonium derivatives are obtained from hydrogen phosphide, PH_3, and alkyl halogen compounds.

2. **ARSINES.** Well-known primary and secondary compounds are: *methylarsenic dichloride*, CH_3AsCl_2 (liquid, b.pt. 135°); *dimethylarsenic chloride*, $(CH_3)_2AsCl$ (b.pt. 100°); *dimethylarsine*, $(CH_3)_2AsH$ (b.pt. 36°); *dimethylarsenic acid* or *cacodylic acid*, $(CH_3)_2AsO \cdot OH$, &c. The tertiary arsines are obtained by the action of sodium arsenide, $AsNa_3$, on alkyl iodides:

$$3C_2H_5I + AsNa_3 = 3NaI + As(C_2H_5)_3;$$

they are liquids slightly soluble in water, with which they do not form bases. The *quaternary arsonium compounds, e.g.* $(CH_3)_4AsI$ (*tetramethylarsonium iodide*), obtained from the tertiary arsines and alkyl iodides, are, however, very energetic and are able to give, with moist silver oxide, *tetramethylarsonium hydroxide*. The *cacodyl*

$$[(CH_3)_2As - As(CH_3)_2]$$

compounds were studied by Bunsen (1837–1843), who obtained *cacodyl oxide*,

$$(CH_3)_2As \cdot O \cdot As(CH_3)_2,$$

by distilling arsenic trioxide with potassium acetate (this reaction serves as a delicate test for acetates in mixtures):

$$As_2O_3 + 4CH_3 \cdot COOK = 2CO_2 + 2K_2CO_3 + [As(CH_3)_2]_2O.$$

With hydrochloric acid, cacodyl oxide gives *cacodyl chloride*, $(CH_3)_2AsCl$.

Many of these cacodyl compounds are liquids which ignite in the air and have nauseating odours ; the cacodyl behaves like a true electro-positive element.

3. Various alkyl derivatives are known of *antimony* (*stibines*), *boron, silicon, bismuth, tin*, &c., but these are of little practical importance.

4. ALKYLMETALLIC (Organometallic) DERIVATIVES. These are obtained from various metallic chlorides or from the metals themselves (Zn, Hg, Mg, Al, &c.) by the action of halogen derivatives of the hydrocarbons. They are generally colourless liquids with low boiling-points, and some of them are violently decomposed by water and ignite in the air. Of importance for many organic syntheses are the *zinc-alkyls* (*see* pp. 32, 96, and 149).

ZINC METHYL : $Zn(CH_3)_2$, is a colourless, highly refractive liquid, sp. gr. 1·39, b.pt. 46°, and has an intense, repulsive odour ; it ignites in the air, forming zinc oxide, and with water gives methane and zinc hydroxide. It is formed in two phases, as follows, and is separated by distillation :

(*a*) $CH_3I + Zn = Zn(CH_3)I$ (*zinc methyl iodide*, solid) ;
(*b*) $2Zn(CH_3)I = ZnI + Zn(CH_3)_2$.

GRIGNARD'S REACTION. Mention has already been made of the use of this reaction in synthesising the saturated hydrocarbons (p. 32). One molecule of a monohalogen (Br or I) compound, in presence of absolute ether, combines with an atom of magnesium : $Mg + C_2H_5Br = C_2H_5MgBr$ (*ethyl magnesium bromide*), and with compounds containing several carbon atoms there is always formed, as a secondary product, a saturated hydrocarbon. The ether probably takes part in the reaction, forming an intermediate product $C_2H_5\cdot Mg\cdot Br[(C_2H_5)_2O]$.

The latter, and also the alkyl magnesium halogen compounds, when dissolved in ether, are highly reactive and form additive compounds with aldehydes, ketones, and even esters of mono- and poly-basic carboxylic acids ; with water these additive compounds then give the corresponding *secondary* and *tertiary alcohols*, the reaction occurring in the following two phases (R = alkyl) :

$$\underset{\text{Aldehyde}}{\mathrm{R\cdot CHO}} + \underset{\text{Alkyl magnesium iodide}}{\mathrm{R'MgI}} = \mathrm{R\cdot C}\begin{cases}\mathrm{O\cdot MgI}\\ \mathrm{R'}\\ \mathrm{H}\end{cases} \rightarrow + \mathrm{H_2O} = \mathrm{I\cdot Mg\cdot OH} + \underset{\text{Secondary alcohol}}{\mathrm{R\cdot CH(OH)\cdot R'}}$$

$$\underset{\text{Ethyl formate}}{\mathrm{H\cdot COOC_2H_5}} + \mathrm{C_2H_5MgBr} = \mathrm{C_2H_5\cdot C}\begin{cases}\mathrm{OMg\cdot Br}\\ \mathrm{H}\\ \mathrm{OC_2H_5}\end{cases} \rightarrow + \mathrm{C_2H_5\cdot MgBr} =$$

$$\mathrm{Br\cdot Mg\cdot OC_2H_5} + \mathrm{C_2H_5\cdot C}\begin{cases}\mathrm{OMgBr}\\ \mathrm{H}\\ \mathrm{C_2H_5}\end{cases} \rightarrow + \mathrm{H_2O} = \mathrm{BrMgOH} + \underset{\text{Diethylcarbinol}}{\mathrm{C_2H_5\cdot CH(OH)\cdot C_2H_5}}$$

If esters of other monobasic acids are used instead of a formic ester, tertiary alcohols are obtained, whilst esters of dibasic acids give dihydric alcohols. Hence, by means of the *Grignard reaction, the carboxylic oxygen of any acid* (starting from the corresponding ester) *is ultimately replaced by two alkyl residues.* Similar behaviour is also shown by acid chlorides and anhydrides, which also contain carbonylic oxygen (—CO—).

With nitriles, *ketonimides* and *ketones* are obtained :

$$\mathrm{R\cdot CN + R'MgI = R\cdot C}\begin{cases}\mathrm{N\cdot MgI}\\ \mathrm{R'}\end{cases} \rightarrow + \mathrm{H_2O} =$$

$$\mathrm{IMgOH + R\cdot C(:NH)\cdot R'} \rightarrow + \mathrm{H_2O = NH_3 + R\cdot CO\cdot R'}\ \text{(ketone).}$$

Further, with dry CO_2, alkyl magnesium compounds give organic acids :

$$\mathrm{R'MgI + CO_2 = R'\cdot COOMg\cdot I} \rightarrow + \mathrm{HX = IMgX + R'\cdot COOH}\ \text{(acid).}$$

Other most varied organic syntheses have been rendered possible of late years by the Grignard reaction.

VI. ALDEHYDES AND KETONES, $C_nH_{2n}O$

The elimination of two atoms of hydrogen by means of an oxidising agent (*e.g.* potassium dichromate and dilute sulphuric acid, or sometimes even the oxygen of the air), from a primary or secondary alcohol yields an aldehyde or a ketone: $R\cdot CH_2\cdot OH + O = H_2O + R\cdot CHO$ (*aldehyde*), or

$$R\cdot CH(OH)R' + O = H_2O + R\cdot CO\cdot R' \text{ (ketone)}.$$

The aldehydes have a strong reducing action, as they fix oxygen and become converted into acids with the same numbers of carbon atoms, whilst the ketones resist oxidising agents, and, if these are very energetic, are oxidised to acids containing fewer carbon atoms than the original ketones.

(*a*) ALDEHYDES

The first members of this series are neutral liquids with pronounced and often disagreeable odours (formaldehyde is a gas) and are soluble in water, whilst the higher ones gradually become solid and insoluble. Their boiling-points are much lower than those of the corresponding alcohols.

The aldehydes are *formed* when a calcium or barium salt (or even two salts) of a monobasic organic acid is dry distilled with calcium or barium formate (reducing agent): $(R\cdot COO)_2Ca + (H\cdot COO)_2Ca = 2CaCO_3 + 2R\cdot CHO$.

They are also obtained on heating with water compounds containing two halogen atoms united to the same carbon atom:

$$CH_3\cdot CHCl_2 \text{ (ethylidene chloride)} + H_2O = 2HCl + CH_3\cdot CHO.$$

The *constitution of the aldehydes* can be deduced from their methods of formation (*e.g.* the latter) and the characteristic aldehyde group is $-C\begin{smallmatrix} \nearrow O \\ \searrow H \end{smallmatrix}$.

PROPERTIES. They are substances of considerable and varied reactivity. With oxidising agents they are transformed into acids, and this reducing property is readily manifested in their reduction of *ammoniacal silver nitrate solution* (22 per cent. ammonia solution and 10 per cent. of dilute silver nitrate diluted with its own volume of 10 per cent. sodium hydroxide solution; or 1 grm. of silver nitrate dissolved in 30 c.c. of water and dilute ammonia added as long as no precipitate forms) or of Fehling's solution (the latter, however, is not reduced by aldehydes containing as many as 8 or 9 carbon atoms).

In their turn, the aldehydes are converted back into the primary alcohols when reduced with nascent hydrogen; with PCl_5, they give ethylidene chlorides again.

Hydrocyanic acid, ammonia, sodium hydrogen sulphite, and sometimes alcohol and acetic anhydride (also the alkyl magnesium halogen compounds: *see above*, Grignard's Reaction) form characteristic *additive products* with the aldehydes:

$$CH_3\cdot CHO + 2C_2H_5\cdot OH \text{ (+ a little HCl)} = H_2O + CH_3\cdot CH(OC_2H_5)_2 \text{ (acetal)},$$

which is an ether of the hypothetical glycol (dihydric alcohol), $CH_3\cdot CH(OH)_2$; the latter, however, does not exist in the free state, since *two hydroxyl groups cannot remain joined to one and the same carbon atom*, excepting in the case of *chloral hydrate* (*see later*) and a very few other substances.[1]

They combine with sodium and ammonium bisulphites (very concentrated

[1] *See* Table on opposite page.

solutions) forming crystalline *bisulphite compounds* soluble in water and slightly so in alcohol :

$$C_2H_5\cdot C\Big\langle{}^{O}_{H} + SO_3HNa = C_2H_5\cdot C\Big\langle{}^{OH}_{H}{-}O\cdot SO_2Na.$$

and these compounds, when heated with dilute acid or with alkali (even Na_2CO_3), liberate the aldehyde again. This reaction hence renders possible the separation of aldehydes from other substances.

The aldehydes combine with ammonia forming crystalline *aldehyde-ammonias* soluble in water and slightly so in alcohol but insoluble in ether, for example, $CH_3\cdot CH(OH)(NH_2)$, which gives the aldehyde again when heated with a dilute acid. But formaldehyde, with ammonia, readily forms polymerised derivatives, *e.g. hexamethylenetetramine,* $(CH_2)_6N_4$.

With hydrocyanic acid they form *cyanohydrins* (p. 199).

An interesting change is the *aldol condensation,* that is, the condensation of 2 mols. of an aldehyde brought about by prolonged heating with dilute mineral acids, dilute alkalis, or even aqueous solutions of sodium acetate. Possibly a molecule of water is first added to one of the aldehydes :

$$CH_3\cdot C\Big\langle{}^{O}_{H} + H_2O = CH_3\cdot CH\Big\langle{}^{OH}_{OH},$$

this hypothetical hydrate then condensing with another molecule of aldehyde, with separation of water and formation of a hydroxyaldehyde (*aldol*) :

$$CH_3\cdot CH\Big\langle{}^{OH}_{OH} + CH_3\cdot C\Big\langle{}^{O}_{H} = H_2O + CH_3\cdot CH(OH)\cdot CH_2\cdot C\Big\langle{}^{O}_{H}$$

(*β-hydroxybutyraldehyde*). These aldols in their turn readily lose a molecule of water, forming an unsaturated aldehyde, which can also be obtained directly (*aldehyde condensation*) by heating the original aldehyde with a dehydrating agent such as zinc chloride :

$$CH_3\cdot C\Big\langle{}^{O}_{H} + CH_3\cdot C\Big\langle{}^{O}_{H} = H_2O + CH_3\cdot CH : CH\cdot C\Big\langle{}^{O}_{H}.$$

DERIVATIVES OF ACETALS

Name	Formula	Boiling-point	Specific gravity
ALKYL DERIVATIVES			
Methylal	$CH_2(OCH_3)_2$	41·3°–41·7° (749·8 mm.)	0·862 (18°)
Diethylmethylal	$CH_2(OC_2H_5)_2$	87°	0·834 (20°)
Dipropylmethylal	$CH_2(OC_3H_7)_2$	136°	0·834 (20°)
Diisopropylmethylal	$CH_2(OC_3H_7)_2$	118°	0·831 (20°)
Diisobutylmethylal	$CH_2(OC_4H_9)_2$	164°	0·824 (20°)
Diisoamylmethylal	$CH_2(OC_5H_{11})_2 + H_2O$	206°	0·835 (20°)
Dihexylmethylal	$CH_2(OC_6H_{13})_2$	174°–175°	0·822 (15°)
Dioctylacetal	$CH_3\cdot CH(OC_8H_{17})_2$	289°	0·848 (15°)
Dimethylacetal	$CH_3\cdot CH(OCH_3)_2$	63°	0·865 (22°)
Diethylacetal	$CH_3\cdot CH(OC_2H_5)_2$	102·9°	0·831 (20°)
Dipropylacetal	$CH_3\cdot CH(OC_3H_7)_2$	147°	0·825 (22°)
Diisobutylacetal	$CH_3\cdot CH(OC_4H_9)_2$	170°	0·816 (22°)
Diisoamylacetal	$CH_3\cdot CH(OC_5H_{11})_2$	211°	0·835 (15°)
ACID DERIVATIVES			
Methylenediacetate	$CH_2(O\cdot CO\cdot CH_3)_2$	170°	—
Ethylenediacetate	$CH_3\cdot CH(O\cdot CO\cdot CH_3)_2$	169°	1·073 (15°)
Ethylenedipropionate	$CH_3\cdot CH(O\cdot CO\cdot C_2H_5)_2$	192°	1·020 (15°)
Ethylenedibutyrate	$CH_3\cdot CH(O\cdot CO\cdot C_3H_7)_2$	215°	0·985 (15°)
Ethylenediisovalerate	$CH_3\cdot CH(O\cdot CO\cdot C_4H_9)_2$	225°	0·947 (15°)

The aldehydes, especially form-, acet-, and prop-aldehydes, &c., exhibit a tendency to *polymerise*, in the mere presence of a little hydrochloric or sulphuric acid, sulphur dioxide, zinc chloride, &c. Acetaldehyde, for example, gives two isomerides: *paraldehyde*, m.pt. 10°, b.pt. 124°, and *metaldehyde*, which sublimes at 100°:

$$3C_2H_4O = CH_3\cdot CH\begin{cases} O\cdot CH(CH_3) \\ O\cdot CH(CH_3) \end{cases}O.$$

These no longer react with ammonia, sodium bisulphite, silver nitrate, and hydroxylamine, but they yield the aldehyde again when distilled in presence of a small quantity of dilute sulphuric acid.

With alkalis, even dilute alkalis, many aldehydes, especially the more simple ones of the fatty series, resinify, whilst some give rise to an alcohol and an acid:

$$2HC\cdot\begin{cases} O \\ H \end{cases}(\textit{formaldehyde}) + H_2O = CH_3\cdot OH + H\cdot CO_2H\ (\textit{formic acid}).$$

With halogens the aldehydes give substitution products, and with hydrogen sulphide various complex products (*thioaldehydes*, &c.) with characteristic odours.

With hydroxylamine, aldehydes form *aldoximes*, which are resolved into their components when boiled with acids, and yield nitriles when treated with dehydrating agents: $CH_3\cdot CHO + NH_2\cdot OH = H_2O + CH_3\cdot CH : N\cdot OH$.

A similar action is exhibited by the hydrazines (as hydrochloride or acetate in acetic acid solution containing sodium acetate; the most suitable is phenylhydrazine), which give characteristic, stable, and often crystalline compounds, termed *hydrazones*:

$$CH_3\cdot CHO + C_2H_5\cdot NH\cdot NH_2\ (\textit{ethylhydrazine}) =$$
$$H_2O + CH_3\cdot CH : N\cdot NH\cdot C_2H_5\ (\textit{acetaldehyde ethylhydrazone});$$

by nascent hydrogen (4H) this is converted into 2 mols. of primary amine:

$$2CH_3\cdot CH_2\cdot NH_2.$$

Characteristic of the aldehydes is also the formation of crystalline *semicarbazones* by the action of the hydrochloride of *semicarbazide*, $NH_2\cdot CO\cdot NH\cdot NH_2$ (obtained by the interaction of potassium cyanate and hydrazine hydrate):

$$R\cdot CHO + NH_2\cdot CO\cdot NH\cdot NH_2 = H_2O + R\cdot CH : N\cdot NH\cdot CO\cdot NH_2.$$

Both the hydrazones and semicarbazones serve for the separation of the aldehydes from other substances and for their quantitative determination.

Finally a characteristic qualitative reaction which is given generally by the aldehydes and is very sensitive is that of Schiff. It consists in shaking the liquid to be tested with a solution (0·02 per cent.) of fuchsine previously decolorised by a current of sulphur dioxide. Traces of an aldehyde produce a reddish violet coloration (it is uncertain if *pure* ketones also give this reaction).

Another reaction characteristic of the aldehydes and not given by ketones is that with benzosulphinehydroxamic acid or with *nitrohydroxylaminic acid*, $OH\cdot NO : N\cdot OH$, which forms *hydroxamic acids*, $R\cdot C\begin{cases} OH \\ N\cdot OH \end{cases}$ the latter producing a cherry-red coloration with ferric chloride.

FORMALDEHYDE (or Methanal), **H·CHO**, is a gas which liquefies at − 20° to a mobile, colourless liquid having the sp. gr. 0·8153 and solidifying at − 92°. It is very soluble in alcohol or water, and is placed on the market

in the form of 40 per cent. aqueous solution [1] under the name of *formalin* or *formol*; the commercial product often contains 12 to 15 per cent. of methyl alcohol to prevent separation of polymerised compounds. Indeed, even in the cold, formaldehyde readily forms *paraformaldehyde*, $(CH_2O)_2$, a white solid soluble in water, or the crystalline *trioxymethylene* (or *metaformaldehyde*), $(CH_2O)_3$. Both of these give the aldehyde when volatilised by heat, and they are used thus as disinfectants under the names *triformol* and *paraformol*. Formaldehyde may also give rise to a mixture of saccharine compounds (*formose*). With ammonia it gives, not an aldehyde-ammonia, but *hexamethylenetetramine*, $C_6H_{12}N_4$, which is crystalline and of feebly monobasic character.[2] With potassium hydroxide it does not resinify, but yields methyl alcohol and formic acid (p. 206).

A question which has been under discussion for many years is the possible formation of formaldehyde as the first product in the natural synthesis of carbohydrates (*see* Sugar) in the leaves of plants, from carbon dioxide under the influence of chlorophyll.

Numerous sensitive reagents have been employed to detect microscopically the transitory formation of formaldehyde in *living* leaves; but almost all these reagents are poisonous to plants and no decisive results have been obtained, even those of Pollacci (1907), who distilled the leaves with water and tested for formaldehyde in the distillate, being doubtful. Schryver (1910) has succeeded in establishing the formation of aldehyde in green plants in sunlight, by making use of a very sensitive reagent (detecting 1 part of aldehyde per million) consisting of a solution of phenylhydrazine, potassium ferricyanide, and hydrochloric

[1] The concentrations of commercial aqueous solutions of formaldehyde can be deduced from the specific gravities by means of the following table (*Auerbach*, 1905):

Sp gr. at $\frac{18°}{4°}$	Grms. of CH_2O in 100 c.c. of solution	Grms. of CH_2O in 100 grms of solution
1 0054	2 24	2 23
1 0090	3 50	3·45
1·0126	4 66	4 60
1·0172	6·51	6·30
1·0218	8·37	8 0
1·0311	11·08	10 74
1·0410	14·15	13 59
1·0568	19 89	18·82
1·0719	25·44	23·73
1·0853	30 17	27 80
1·1057	37·72	34·11
1·1158	41·87	37·53

If the aldehyde is pure and leaves no residue, the percentage by volume, if greater than 23, should be increased by about 5.

The analysis of commercial formalin is based on the following reaction of Blank and Finkenbeiner: $2CH_2O + 2NaOH + H_2O_2 = H_2 + 2H_2O + 2H{\cdot}CO_2Na$. Three grammes of the formaldehyde solution are poured into a long-necked flask containing 25 c.c. of 2N-caustic-soda solution (free from carbonates), the liquid being mixed and 50 c.c. of hydrogen peroxide solution (neutralised or of known acidity) carefully added, 3 minutes being taken to make this addition. After 7 to 8 minutes, the excess of alkali remaining is titrated with 2N-sulphuric acid. With every cubic centimetre of the 2N-alkali that has reacted corresponds 0·06 grm. of formaldehyde. Litmus purified several times with alcohol should be used as indicator.

The estimation of the aldehyde may also be carried out with ammonia (*see succeeding* Note).

Brautigam (1910) suggested determining formaldehyde by adding to it excess of clear calcium hypochlorite solution. After a time the solution deposits calcium carbonate, which is filtered, washed, and weighed; 1 mol. of $CaCO_3$ corresponds with 1 mol. of formaldehyde.

To determine the *methyl alcohol* which may be present, 5 c.c. of the solution, diluted with 100 c.c. of water, are distilled with an excess of ammonia (about 10 c.c. of concentrated ammonia), 50 c.c. of the distillate being collected in a 100 c.c. flask and made up to volume with water. The methyl alcohol in 5 c.c. of this solution, which contains only negligible traces of formaldehyde, is determined by the iodine method (*see* p. 107).

[2] This reaction was proposed by L. Leger in 1883 as a means of estimating formaldehyde in commercial solutions: $6CH_2O + 4NH_3 = (CH_2)_6N_4 + 6H_2O$; the reaction is, however, slow and the method not very accurate. F. Hermann (1911) has rendered it more rapid and exact in the following manner. Four cubic centimetres of the formalin are weighed into a 150 c.c. flask with a ground stopper, and about 3 grms. of pure powdered ammonium chloride and exactly 25 c.c. of 2N-caustic soda (equivalent to 50 c.c. of normal soda) added. The flask is stoppered and shaken, and, when the mass is cool, 50 c.c. of water and 4 drops of 1 per cent. methyl orange are added and the excess of alkali titrated with normal sulphuric acid. Deduction of the volume of acid required from 50 c.c. gives the volume of soda used in liberating, from the ammonium chloride, a corresponding amount of nascent ammonia, which instantly transforms the aldehyde into hexamethylenetetramine. The latter is, however, monobasic and reacts with part of the sulphuric acid, and, in order to obtain the number of grammes of formaldehyde in the quantity of formalin taken, the number of cubic centimetres of soda arrived at above must be multiplied by the factor 0·06. If the formalin be acid initially, the acidity must be determined separately by titration with soda in presence of phenolphthalein and the 50 c.c. of soda increased accordingly.

acid ; this reagent gives a magenta-red coloration with formaldehyde or with the methylene derivative which chlorophyll would form with the aldehyde.

MANUFACTURE. Formaldehyde is obtained by passing a mixture of methyl alcohol vapour and air over copper or platinum gauze or the finely divided metals, which act as catalysts (O. Blank, Ger. Pat. 228,697, 1908, obtained quantitative yields by using silver precipitated on asbestos). The product is rectified in a column filled with pieces of clay. Patents have been taken out for the preparation of formaldehyde by the oxidation of methane with oxide of iron, hydrogen peroxide, &c. It is also formed by the electrolysis of dilute methyl alcohol, and some years ago a patent was granted for its preparation by passing a mixture of formic acid vapour and hydrogen through a tube containing pieces of metal (*e.g.* lead, iron, zinc, nickel, silver, &c.), heated to 300°.

Formaldehyde has considerable antiseptic power, even in aqueous solution. It is largely used at the present time as a disinfectant in houses and for the preservation of readily putrescible substances (meat, beverages, &c.). Its vapour has an acute and penetrating odour and irritates the eyes. On account of the property possessed by formaldehyde of combining with proteins to form insoluble and stable products, it is used in the manufacture from casein of articles of a horny consistency and in making imitation pegamoid; also in preparing photographic films with gelatine, for rendering insoluble or hardening the coloured gelatine for textile printing, and for hastening the tanning of skins.

Owing to its great reactivity, it is largely used in organic syntheses, *e.g.* in the manufacture of aniline dyes.

Various solid and liquid disinfectants containing free aldehyde are prepared by means of soaps (soap solutions are also on the market under the names of *lysoform* and *ozoform*, the starting product in the case of the latter being sulphoricinoleic acid).

A characteristic and very sensitive reaction of formaldehyde is that proposed by Rimini, according to whom a mixture of phenylhydrazine hydrochloride, sodium nitroprusside and caustic soda is coloured blue even by minimum traces of the aldehyde.

Formaldehyde gives Schiff's reaction even in presence of a certain amount of sulphuric acid, whilst acetaldehyde does not.

The price of commercial 40 per cent. formaldehyde is about £4 per quintal, while pure, powdered paraldehyde costs 4*s*. to 5*s*. per kilo.

ACETALDEHYDE (Ethanal), $CH_3 \cdot CHO$, is a colourless, mobile liquid, sp. gr. 0·801 (at 0°), b.pt. 21°, and solidifies at −121°. It has an agreeable but suffocating odour, and it polymerises with moderate ease, giving the *paraldehyde* and *metaldehyde* (*see above*). It dissolves in water, alcohol, or ether, and is readily converted into acetic acid by oxidising agents.

It is prepared by pouring a mixture of 3 parts of 90 per cent. alcohol and 4 parts of concentrated sulphuric acid slowly into a solution of 3 parts of potassium bichromate in 12 of water, the liquid being kept cool meanwhile. The solution is then heated in a reflux apparatus on a water-bath and subsequently distilled. The mixture of alcohol, aldehyde, and acetal thus obtained is heated to 50° and the aldehyde vapour passed into cold ether. On passing ammonia into this solution, crystallised aldehyde-ammonia, $CH_3 \cdot CH(OH) \cdot NH_2$, separates ; this, when pressed and distilled with dilute sulphuric acid, gives pure acetaldehyde. The *commercial aldehyde* is obtained from the foreshots of alcohol distillation, from which it is separated by simple fractional distillation.

It is of importance in many organic syntheses and in the production of silver mirrors. The price of 50 per cent. solutions is 2*s*. per kilo, that of the 95 to 99 per cent. product 3*s*. 6*d*., and that of the purest aldehyde 15*s*.[1]

[1] The *estimation* of acetaldehyde is based on the following reaction (Seyewetz and Bardin) :

$$2Na_2SO_3 + 2CH_3 \cdot CHO + H_2SO_4 = Na_2SO_4 + (CH_3 \cdot CHO, NaHSO_3)_2.$$

The aldehyde is diluted to 7 to 8 per cent. and about 10 c.c. of this solution is poured into 40 c.c. of 10 per cent. pure sodium sulphite solution. After the addition of a few drops of neutralised alcoholic phenolphthalein solution

METHYLAL, $H \cdot CH(OCH_3)_2$, and ACETAL, $CH_3 \cdot CH(OC_2H_5)_2$ (see p. 204).

PROPALDEHYDE, $C_2H_5 \cdot CHO$, is found among the tarry products from the distillation of wood. Valeraldehyde, $C_4H_9 \cdot CHO$, boils at 92° and begins to show a diminution in solubility in water. Normal heptaldehyde (*œnantaldehyde*), $C_6H_{13} \cdot CHO$, is found among the products of decomposition of castor oil when this is subjected to distillation in a vacuum. Nonyl aldehyde, $C_8H_{17} \cdot CHO$, occurs in the oxidation products of oleic acid or, better, in the decomposition products of the ozonide of oleic acid (Harries, Molinari, &c.); it boils at about 192°.

CHLORAL (Trichloroethanal), $CCl_3 \cdot CHO$, is the most important halogenated derivative of the aldehydes. It is a dense liquid with a peculiar, penetrating odour and boils at 94·4°. It is prepared by passing chlorine into pure alcohol (96 per cent.) for some days, the hydrochloric acid formed being collected. The liquid is then heated with sulphuric acid in a reflux apparatus until no further evolution of hydrogen chloride occurs, the chloral being distilled and subsequently purified by rectification. Within recent times it has also been prepared electrolytically: the bath contains potassium chloride solution at 100° and is fitted with a diaphragm; alcohol is passed into the anode chamber, where chlorine is formed, and the hydrogen chloride produced at the anode is neutralised by the potassium hydroxide formed (1 h.p.-hour yields 50 grms. of chloral).

Chloral gives the reactions of the aldehydes and is used in medicine as an anæsthetic and soporific, being first treated with water to form the crystalline CHLORAL HYDRATE, $CCl_3 \cdot CH{<}^{OH}_{OH}$, which is readily soluble in water (m.pt. 57°); this is one of the few compounds having two hydroxyl groups united to the same carbon atom. The crystalline alcoholates or Acetals, $CCl_3 \cdot CH(OH) \cdot OC_2H_5$ and $CCl_3 \cdot CH(OC_2H_5)_2$, corresponding with this hydrate are known.

Chloral costs about 6*s*. per kilo.

ALDEHYDES WITH UNSATURATED RADICALS

ACRYLIC ALDEHYDE (Propenal, Acrolein, or Allyl Aldehyde), $CH_2 : CH \cdot CHO$, is formed when fats are burned, owing to loss of water by the glycerol present; a similar change takes place when glycerol is heated with potassium hydrogen sulphate or boric acid. Acroleïn, which can also be obtained by the oxidation of allyl alcohol, is a liquid, b.pt. 52·4°, and has a characteristic pungent odour. When oxidised, it yields acrylic acid and, when reduced, allyl alcohol. It has all the chemical properties of the aldehydes and polymerises in the course of a few hours. With ammonia, it gives a solid, basic condensation product, soluble in water: $2C_3H_4O + NH_3 = H_2O + C_6H_9ON$ (*acroleïn-ammonia*, which gives *picoline* on distillation). Owing to its double linking, acroleïn unites with 2 mols. of sodium bisulphite and the resulting product, when boiled with acid, gives up only one bisulphite molecule, namely, that combined with the aldehyde group.

CROTONIC ALDEHYDE, $CH_3 \cdot CH : CH \cdot CHO$, is obtained by distilling the corresponding aldol, $CH_3 \cdot CH(OH) \cdot CH_2 \cdot CHO$, at 140° or by the dehydrating action of zinc chloride or sodium acetate on the saturated aldehyde. It is a liquid boiling at 104° and possessing a penetrating odour, and its constitution is shown by the fact that it yields crotonic acid when oxidised with silver oxide.

CITRAL (or Geranial), $(CH_3)_2C : CH \cdot CH_2 \cdot CH_2 \cdot C(CH_3) : CH \cdot CHO$, is a liquid of pleasant odour, b.pt. 229°, and occurs in many essences (of mandarin, citron, lemon, orange, and most abundantly—60 per cent.—in that of *Verbena indiana* or lemon-grass, from which it is separated by means of its bisulphite compound). It may also be obtained by the gentle oxidation of the corresponding alcohol, *gerianol*, which boils at 230°. It exists in two stereoisomeric forms, the cis- and trans-modifications. When oxidised with potassium bisulphate at 170°, citral is transformed into *cymene* (with a closed ring) with separation of water.

the liquid is cooled to 4° to 5° and titrated with normal sulphuric acid until it is decolorised. This occurs when no further combination of aldehyde and sulphurous acid takes place. This determination is not affected by the presence of alcohol, acetal, or paraldehyde.

CITRONELLAL, $(CH_3)_2C : CHC\cdot H_2\cdot CH_2\ CH(CH_3)\cdot CH_2\cdot CHO$, is found with citral in citron oil and boils at 208°.

PROPARGYL ALDEHYDE, $CH : C\ CHO$, is a solid, m.pt. 60°, and is obtained from dibromoacrolein by way of the acetal. As it contains the group $CH : C$, it forms metallic derivatives (*see* p. 91).

(*b*) KETONES (R—CO—R′)

These have the carbonyl group attached to two alcohol radicals and, if the latter are similar, are known as *simple ketones* and, if different, *mixed ketones.* The first member must contain at least three carbon atoms. They present the same cases of isomerism as the secondary alcohols, and are metameric with the aldehydes.

Up to the C_{11}-compound they are liquid and beyond that solid, but all are less dense than water. They resist feeble oxidation but energetic oxidising agents (dichromate and dilute sulphuric acid) break the chain of the ketone at the carbonyl group, thus forming an acid with a lower number of carbon atoms: $CH_3\cdot CO\cdot CH_3 + 4O = H_2O + CO_2 + CH_3\cdot CO_2H$. In mixed ketones, however, the carboxyl is mainly united to the smaller alkyl radical (R or R′), but the acid with the higher alkyl is always formed to some extent. With ammonia, the action is different from that in the case of aldehydes: water is eliminated from 2 or 3 mols. of ketone and *di-* and *tri-ketonamines* (or *acetonamines*), *e.g.* $C_6H_{13}ON$, formed Further, the ketones do not polymerise, but they form condensation products. They do not react with ammoniacal silver solutions or with Fehling's solution, and are hence not reducing in character (difference from aldehydes).

With phosphorus pentachloride they give the corresponding dichloro-derivatives; for instance, acetone gives 2-dichloropropane, $CH_3\cdot CCl_2\cdot CH_3$.

On reduction, they yield secondary alcohols, and with very energetic oxidising reagents (H_2O_2, &c.), they form *characteristic* polymerised ketonic peroxides, *e.g.* $[(CH_3)_2CO_2]_2$, $[(CH_3)_2CO_2]_3$. With ethyl orthoformate they give *acetals*, $(CH_3)_2C(OC_2H_5)_2$, and similarly with mercaptans they form Mercaptols, *e.g.* $(CH_3)_2C(SC_2H_5)_2$, which, when oxidised with permanganate, gives Sulphonal, $(CH_3)_2C(SO_2C_2H_5)_2$.

Ketones, which generally contain the group $CH_3\cdot CO\cdot$ form, with sodium bisulphite, compounds which are crystalline and hence readily separable from other substances:

$$(CH_3)_2CO + SO_3HNa = (CH_3)_2C{<}{\substack{OH \\ SO_3Na}}\ (\textit{sodium acetonebisulphite}).$$

This compound crystallises also with 1 mol. H_2O and yields acetone easily when heated with dilute soda solution.

With hydrocyanic acid, ketones give the *cyanohydrins* or nitriles of higher acids: *e.g.* $(CH_3)_2C{<}{\substack{OH \\ CN}}$.

With hydrogen sulphide, but *only* in presence of HCl, &c., they form *trithioketones*, which on heating give simple *thioketones*.

With hydroxylamine, ketones readily form the so-called *ketoximes*, $R_2C : N\cdot OH$,[1] similar to aldoximes, and with phenylhydrazine they give phenylhydrazones, just as aldehydes do:

$$(CH_3)_2CO + NH_2\cdot OH = H_2O + (CH_3)_2C : N\cdot OH\ (\textit{acetoxime}).$$

[1] For the *ketoximes* (as for the *aldoximes*) stereoisomerides exist as a consequence of the *stereoisomerism of nitrogen* (*see* p. 22), which has been studied by Beckmann, V. Meyer, Auwer, H. Goldschmidt, Hantzsch and Werner, Minunni, &c. Thus for aldoximes we have the two following stereoisomeric configurations:

$$\begin{array}{c} R—C—H \\ \| \\ N—OH \end{array}\ (\textit{syn}\text{-aldoxime}) \text{ and } \begin{array}{c} R—C—H \\ \| \\ OH—N \end{array}\ (\textit{anti}\text{-aldoxime}),$$

Under certain conditions, *e.g.* by the action of acetyl chloride, ketoximes undergo an atomic transposition by which they are converted into amides, substituted in the amino-group (Beckmann rearrangement), these being tautomeric with the ketoximes :

$$\begin{array}{c} R\cdot C\cdot R' \\ \| \\ N\cdot OH \end{array} \rightarrow \begin{array}{c} R\cdot C : O \\ | \\ NHR'. \end{array}$$

The action of nitrous acid (or its esters) yields *isonitrosoketones :*

$$CH_3\cdot CO\cdot CH_3 + NO_2H = H_2O + CH_3\cdot CO\cdot CH : N\cdot OH.$$

In presence of various reagents, *e.g.* lime, potash, sulphuric or hydrochloric acid, &c., the ketones lose water and undergo *condensation* (whilst aldehydes polymerise): $3(CH_3)_2CO = 2H_2O + C_9H_{14}O$. Similar condensations occur between ketones and aldehydes.

The **FORMATION OF KETONES** takes place in the dry distillation of wood or of the calcium or barium salts of many organic acids or on simple heating of the latter or the anhydrides of the acids in presence of phosphorus pentoxide: $(CH_3\cdot CO_2)_2Ca = CaCO_3 + CH_3\cdot CO\cdot CH_3$ (*acetone*); if *mixed ketones* are required, a mixture of the salts of two different acids is used.[1] Noteworthy also is the formation of ketones by the oxidation of secondary alcohols (*see* p. 103): $CH_3\cdot CH(OH)\cdot CH_3 + O = H_2O + CH_3\cdot CO\cdot CH_3$. Also, with powdered metals (Sabatier and Senderens, p. 34), secondary alcohols give ketones, hydrogen being eliminated.

Ketones are also formed by the action of water in the hot on chlorinated hydrocarbons having two chlorine atoms united to the same carbon atom: $(CH_3)_2CCl_2 + H_2O = 2HCl + CH_3\cdot CO\cdot CH_3$.

Another general method of preparing ketones is based on the interaction of zinc alkyls and acid chlorides, the additive product formed being immediately decomposed with water so as to avoid the formation of tertiary alcohols: $2CH_3\cdot CO\cdot Cl + Zn(C_2H_5)_2 = ZnCl_2 + 2CH_3\cdot CO\cdot C_2H_5$ (*methyl ethyl ketone*).

Acetone is formed when acetic acid vapour is passed over a heated acetate or base.

ACETONE (**Propanone**), $CH_3\cdot CO\cdot CH_3$, is found in small quantities in the human organism, where it is formed in larger amounts during certain diseases (diabetes, acetonuria). It is formed in considerable quantities in the dry distillation of wood and of other organic substances (calcium acetate, sugar, gum, wool-fat, &c.). It is a liquid with an ethereal odour and a characteristic burning taste, b.pt. 56·3°, sp. gr. 0·7921 at 18°. It solidifies at −94° and is soluble in water (from which it separates on addition of soluble salts), alcohol, ether, and chloroform; it dissolves fats, resins, ethereal oils, nitrocellulose, &c., and is readily inflammable.

In aqueous solution rendered alkaline with sodium carbonate, it is oxidised with ease by potassium permanganate, and chromic acid converts it into acetic acid and carbon dioxide. With sodium it forms *sodium β-allyloxide :*

$$CH_3\cdot C(ONa) : CH_2.$$

whilst for ketoximes, stereoisomerides exist if the two alkyl radicals are different:

$$\begin{array}{c} R—C—R' \\ \| \\ N—OH \end{array} \; (syn\text{-ketoxime}) \text{ and } \begin{array}{c} R—C—R' \\ \| \\ OH—N \end{array} \; (anti\text{-ketoxime})$$

These isomerides are transformable one into the other, and in addition to their physical differences exhibit also chemical differences, *e.g.* in regard to the readiness with which they lose water (aldoximes giving nitriles).

[1] This reaction can be used to demonstrate the *normal constitution* (absence of branching from the carbon chain) of acids, ketones, and hydrocarbons (paraffins), since on distilling an organic barium salt with a normal C_n chain with barium acetate, a C_{n+1} ketone is obtained which should also be normal, as the methyl group of the acetate unites with the carbonyl at the end of the chain of the acid. On oxidation, this ketone gives a C_{n-1} acid which will also be normal. From this are prepared the ketone and then a C_{n-2} acid, so that normal products are always obtained (also the corresponding hydrocarbons) by this gradual descent from a high acid of which the constitution is known to be normal.

In the crude form, it is used in lac and colour factories and in a more or less pure state in the manufacture of iodoform. Also at the present time pure acetone is employed in large quantities for gelatinising smokeless powders and, owing to the intense burning taste it imparts, as a denaturant for spirit, from which it cannot be separated by distillation.

Industrial Preparation. Calcium acetate obtained from pyroligneous acid (*which see*) is subjected to dry distillation, the temperature being controlled so that it does not exceed 300° ; the vapours evolved are rapidly cooled and condensed, giving crude acetone. In order to avoid superheating and irregularity during the distillation, moist calcium acetate is sometimes employed. The acetone vapour escaping condensation is easily recovered by passing it through towers down which a spray of sodium bisulphite solution falls ; this fixes the acetone, which can be liberated by distilling the solution in presence of an alkali. In France, Buisine has utilised the wash-waters of dirty wool to prepare acetone from the fat they contain. This process has been tried on an industrial scale at Roubaix, but as yet without marked success.

The crude acetone is purified by digesting it with quicklime and then distilling it from sodium hydroxide and subsequently over sodium sulphite.

Crude, impure acetone (*oil of acetone*) is sold at £3 8*s*. per quintal if dark or £4 if pale. Acetone for industrial purposes (85 to 90 per cent.) sells at £6, the pure product at £6 16*s*., and the chemically pure (98 to 100 per cent.) at £7 8*s*. per quintal. The bisulphite compound is also placed on the market at £4 per quintal (or 14*s*. per kilo for the chemically pure). In 1908 England consumed 1500 tons of acetone (worth £100,000), which was almost all imported from the United States. In 1910 England imported 1100 tons of acetone, of the value of £57,000. In 1910 Italy imported 438 hectols. of the value of £2600.

Tests for Acetone. These are of especial importance for explosive factories, where a highly purified product is required. It should dissolve in water in all proportions without rendering it turbid. When mixed with a little 0·1 per cent. permanganate solution it should retain the colour for some minutes. If acetone contains water, when mixed with an equal volume of light petroleum (boiling at 40° to 60°) two layers are formed ; if no water is present, the liquids mix perfectly. At least 95 per cent. of it should distil between 56° and 56·5°, and it should not redden blue litmus paper. Kramer's quantitative iodometric test (*see* p. 107) should indicate at least 98 per cent. of acetone ; Strache's method, in which phenylhydrazine is employed, may also be used.[1] The detection of acetone in other substances is effected by means of orthonitrobenzaldehyde and caustic soda, which convert acetone into indigo.

MESITYL OXIDE, $CH_3 \cdot CO \cdot CH : C(CH_3)_2$, is an aromatic liquid boiling at 132°.

PHORONE, $(CH_3)_2C : CH \cdot CO \cdot CH : CMe_2$, forms yellow, readily fusible crystals, and is obtained by saturating acetone with hydrogen chloride.

BUTANONE (Methyl ethyl ketone), $CH_3C \cdot O \cdot C_2H_5$, is a liquid, b.pt. 81°, and is contained in wood-spirit.

KETENES

These constitute a group of substances discovered by Staudinger since 1905. Although they contain the ketonic group, CO, they differ markedly from the ketones in their great reactivity, since they are unsaturated compounds, that is, unsaturated ketones.

They are derived from the type $R_2C : CO$, which was formerly thought incapable of existing in the free state. The residues, R, may be either aromatic or aliphatic hydrocarbon radicals. All these compounds can be derived from **KETENE, $CH_2 : CO$**, which is a colourless gas, b.pt. −56°, m.pt. −151°, and was prepared in 1908 ; it has a disagreeable odour (resembling somewhat those of chlorine and acetic anhydride), is poisonous and even in small quantity produces intense headache. It is easily polymerised (by metallic chlorides or tertiary bases), yielding a coloured resin. It decolorises ethereal bromine solutions

[1] *Strache's method for the indirect estimation of compounds containing carbonyl groups* (*aldehydes and ketones*). When to a solution of an aldehyde or a ketone is added an excess of a phenylhydrazine solution of definite strength, the excess of the latter which does not combine may be deduced from the amount of nitrogen liberated on decomposing (oxidising) in the hot with *Fehling's solution* [a mixture in equal volumes of the following two solutions : (*a*) 69·26 grms. of air-dried copper sulphate crystals dissolved in water to 1 litre ; (*b*) 346 grms. of Rochelle salt dissolved in 800 c.c. of water + 105 grms. sodium hydroxide, the whole made up to 1 litre with water] : $C_6H_5NH \cdot NH_2 + O = H_2O + C_6H_6 + N_2$ The test is made on 0 2 to 0 6 grm. of substance (aldehyde or ketone) and the details of the operation are described in *Zeitschr fur analyt. Chemie*, 1892, p. 573, or in Hans Meyer's "Determination of Radicals in Carbon Compounds," 1899, p. 65.

instantly, and, unlike disubstituted ketenes, does not undergo oxidation in the air. The most stable and best characterised of these compounds are *dimethyl-*, $(CH_3)_2C:CO$, and *diphenyl-ketene,* $(C_6H_5)_2C:CO$; monomethyl-, $CH_3\cdot CH:CO$, and monoethyl-ketene, $C_2H_5\cdot CH:CO$, have properties similar to those of *carbon suboxide,* $O:C:C:C:O$, and resemble the isocyanates in their great reactivity. The disubstituted ketenes are coloured and readily oxidise in the air; two molecules condense with one of a base (pyridine, quinoline), and they unite with the $C:N\cdot$ group (benzylideneaniline) and with the $C:O$ group (quinones), forming β-lactams and β-lactones. All the ketenes combine with water, alcohols, or amines at the double carbon-linking, giving compounds of an acid nature. The monosubstituted ketenes are also called *aldoketenes* and the disubstituted ones, *ketoketenes*. They are usually prepared by the action of zinc on an ethereal solution of acid halogen derivative with a second halogen in the α-position:

$$\underset{\alpha\text{-bromopropionyl bromide}}{CH_3\cdot CHBr\cdot COBr} + Zn = ZnBr_2 + CH_3\cdot CH:CO.$$

The ketenes are easily transformed into acids; and those that condense (the ketoketenes) with unsaturated groups (ethylene and carbonyl compounds, Schiff's bases, thioketones, nitroso- and azo-compounds) form compounds with a closed chain of four or six carbon atoms, these being resolved into two unsaturated compounds when heated. The aldoketenes undergo polymerisation more readily, giving derivatives of cyclobutane which decompose on heating.

B. DERIVATIVES OF POLYHYDRIC ALCOHOLS

The *ethers* of polyhydric alcohols are generally prepared by the methods used for ethers of the monohydric alcohols and have many properties in common with these.

ETHYL ETHER OF GLYCOL, $OH\cdot C_2H_4\cdot OC_2H_5$, boils at 127° and the DIETHYL ETHER, $C_2H_4(OC_2H_5)_2$, at 123°. Of the esters of glycol, the mono- and di-acetates, $C_2H_4(OC_2H_3O)_2$, which are liquids soluble in water, are well known. **Glycolchlorohydrin** or **Monochloroethyl Alcohol**, $OH\cdot CH_2\cdot CH_2\cdot Cl$, boils at 130°, is soluble in water and is prepared by passing hydrogen chloride into hot glycol. GLYCOLSULPHURIC ACID, $OH\ C_2H_4\cdot O\cdot SO_3H$, is the sulphuric ester of glycol. **Glycol Dinitrate**, $C_2H_4(NO_3)_2$, is a yellowish liquid insoluble in water and explode son heating; it is prepared by treating glycol with nitric-sulphuric mixture (*see later,* Nitroglycerine). It is readily hydrolysed by alkali.

ETHYLENECYANOHYDRIN, $CH_2:C:N\cdot CH_2\cdot OH$, is isomeric with **Ethylidenecyanohydrin**, $CH_3\cdot CH(OH)\cdot CN$. **Ethylene Cyanide**, $C_2H_4(CN)_2$, obtained by the action of potassium cyanide on ethylene bromide, forms a crystalline mass; on hydrolysis it gives **Succinic Acid**, $C_2H_4(COOH)_2$.

ETHYLENE OXIDE, $CH_2\cdot O\cdot CH_2$, isomeric with acetaldehyde, is a liquid with an ethereal odour, sp. gr. 0·898 (at 0°), b.pt. 12·5°; although neutral in its reaction it precipitates certain metallic hydroxides from solutions of their salts. It is formed on distilling glycolchlorohydrin with potash. It reacts readily and dissolves in water with gradual formation of glycol.

The following compounds are also known: *Ethylene Monothiohydrate*, $C_2H_4(OH)\ SH$; *Glycol Mercaptan* (*Ethan*-1 : 2-*dithiol*), $C_2H_4(SH)_2$; *Dithioglycol Chloride*, $(C_2H_4Cl)_2S$, which is a very poisonous liquid. *Hydroxymethylsulphonic Acid*, $CH_2(SO_3H)\cdot OH$, is solid and is obtained from methyl alcohol and fuming sulphuric acid. *Methylenedisulphonic* (or *Methionic*) *Acid*, $CH_2(SO_3H)_2$, is formed from acetylene and fuming sulphuric acid, by way of *Acetaldehydedisulphonic Acid*, $CHO\cdot CH(SO_3H)_2$, which with lime gives formic acid and methionic acid; the latter is isomeric with ethylsulphuric acid, but cannot be hydrolysed. *Hydroxyethylsulphonic Acid*, $OH\cdot CH_2\cdot CH_2\cdot SO_3H$ (*Isethionic Acid*), is a crystalline mass formed by treating ethyl alcohol with sulphur trioxide; ethylene with SO_3 gives *Carbyl Sulphate*, $C_2H_4(SO_3)_2$, which forms sulphuric and isethionic acids with water.

Glycol forms also two *amines: Hydroxyethylamine*, $OH\cdot C_2H_4\cdot NH_2$ (primary monovalent base, or *Hydroxyalkyl Base*, or *Hydramine*), and *Ethylenediamine*, $C_2H_4(NH_2)_2$ (primary divalent base). These may also be regarded as derived from one or two molecules of ammonia, in which all or part of the hydrogen is substituted by the hydroxyethyl group, $\cdot C_2H_4\cdot OH$, or by ethylene, $C_2H_4{<}$. Thus, such compounds as the following are known: $NH_2\cdot C_6H_4\cdot OH$; $(NH_2)_2C_2H_4$; $NH(C_2H_4\cdot OH)_2$, *Dihydroxydiethylamine*; $N(C_2H_4\cdot OH)_3$,

Trihydroxytriethylamine; $(NH)_2(C_2H_4)_2$, *Diethylenediamine;* $N_2(C_2H_4)_3$, *Triethylenediamine;* and finally quaternary bases containing alkyl groups, *e.g.* *Choline* (or *Bilineurine*), $(CH_3)_3 : N(\cdot OH)\ C_2H_4 \cdot OH$, or *Hydroxyethyltrimethylammonium Hydroxide*, which is obtained from trimethylamine and ethylene oxide and is found in the bile, in egg-yolk, and in the brain in the form of lecithin (*see later*); it is not poisonous, but when oxidised with nitric acid yields *Muscarine*, $CH(OH)_2 \cdot CH_2 \cdot N(CH_3)_3 \cdot OH$, which has a distinct poisonous action. On putrefaction, choline gives *neurine* (or *Trimethylvinylammonium hydroxide*), $N(CH_3)_3(C_2H_3) \cdot OH$, which is also poisonous. Many of these compounds are formed in putrefying proteins and in dead bodies, and are called *ptomaines*.

These bases are prepared by the same methods as the monovalent bases (p. 200), the primary diamines, for example, being obtained by reducing the nitriles, $C_nH_{2n}(CN)_2$, in hot alcoholic solution by means of sodium or from ethylene bromide and alcoholic ammonia at 100°. They are liquid or solid substances and have certain of the characters of ammonia. *Pentamethylenediamine* or *Cadaverine*, $NH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2\ CH_2 \cdot CH_2 \cdot NH_2$, boils at 179° and, being a δ-diamine, can form *Piperidine*, $C_5H_{11}N$, with separation of ammonia. *Diethylenediamine* or *Piperazine*, $C_2H_4{<}\substack{NH \\ NH}{>}C_2H_4$, melts at 104° and boils at 146°. *Tetramethylenediamine* is called also *Putrescine*.

TAURINE (Aminoethylsulphonic Acid), $NH_2 \cdot CH_2 \cdot CH_2 \cdot SO_3H$, is found in combination with cholic acid (as *Taurocholic Acid*) in the bile of various animals and also in the lungs and kidneys. It forms monoclinic prisms soluble in hot water but insoluble in alcohol, and has a neutral reaction, the basic and acid groups neutralising one another. It is not hydrolysable.

Of the derivatives of *Glycerol*, the *Chlorhydrins* or esters of hydrochloric acid are of interest; they are liquids soluble in alcohol or ether, and, to a less extent, in water. With hydrochloric acid, glycerol forms the *Monochlorhydrin*, $C_3H_5(OH)_2Cl$, of which two isomerides (α- and β-) are known, and the *Dichlorhydrin*, $C_3H_5(OH)Cl_2$, also existing in two isomeric forms. Either of these, when treated with PCl_5, gives the *trichloro*-derivative, $C_3H_5Cl_3$.[1] At the present time interest attaches also to the *formins* and *acetins*, which are used in the manufacture of non-congealing explosives.[2]

GLYCIDE ALCOHOL, $\underbrace{CH_2—CH}_{O} \cdot CH_2 \cdot OH$, is a liquid, b.pt. 162°, soluble in alcohol or ether, and also in water, with which it gives glycerol again; with hydrochloric acid it gives the chlorhydrin. It may be regarded as derived from glycerol by the removal of a molecule of water, and is prepared by the separation of HCl from the α-monochlorhydrin by means of baryta. It is isomeric with propionic acid and reduces ammoniacal silver solution. Separation of hydrogen chloride from the dichlorhydrin yields **Epichlorhydrin**, $\underbrace{CH_2—C}_{O} \cdot HCH_2Cl$, which may be regarded as the hydrochloric ester of glycide alcohol. It boils at 117°, has an odour like that of chloroform and is insoluble in water. It is isomeric with propionyl chloride and monochloroacetone.

GLYCEROPHOSPHORIC ACID, $OH \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot O \cdot PO(OH)_2$, is optically active, as also are its calcium and barium salts (lævo-rotatory). It is interesting from the fact that when the hydroxyl-groups are esterified with palmitic, stearic, or oleic acid, and

[1] According to Ger. Pat. 180,668, the monochlorhydrin is made by heating for 15 hours in an autoclave at 120° a mixture of 100 parts of glycerol with 150 parts of hydrochloric acid (sp. gr. 1 185). The water is distilled off and the residue subjected to fractional distillation in a vacuum (15 mm pressure); after the acid and water have been eliminated, the monochlorhydrin distils over at 130° to 150°, and the unaltered glycerine at 165° to 180°. If it is to be nitrated and used for explosives, it is sufficient to get rid of the water and acid. According to Fr. Pat. 370,224, the monochlorhydrin may also be obtained by shaking glycerine with the calculated quantity of sulphur chloride at a temperature of 40° to 50°; the water formed is distilled off in a vacuum at 60° to 70° The *a-Monochlorhydrin*, $CH_2Cl \cdot CH(OH) \cdot CH_2 \cdot OH$, is obtained (according to Fr. Pat. 352,750) by passing hydrogen chloride into glycerine heated to 70° to 100°.

Like glycerine itself, the chlorhydrins are easily nitrated, yielding non-congealing explosives (*see later*).

[2] Monoacetin, $C_3H_5(OH)_2(O \cdot COCH_3)$, is obtained by heating for 10 to 15 hours at 100° a mixture of 10 parts of glycerol with 15 parts of 40 to 100 per cent. acetic acid, the weak acetic acid (25 to 30 per cent) that distils over being condensed separately. Ten parts of 70 per cent. acetic acid are then added and the weak acid—up to 40 per cent., which distils at 120°—collected apart. After this the temperature is raised in 3 hours to 250°, the weak acid still being kept separate. The crude monoacetin remaining contains about 44 per cent. of combined acetic acid and about 0·8 per cent. of the free acid. This acetin is soluble in water and serves well for the manufacture of explosive and non-congealing nitroacetins (*see* Explosives) and for gelatinising the nitrocellulose of smokeless powders (Vender Ger. Pat 226,422, 1906).

the phosphoric residue united to choline, it gives rise to the important group of *lecithins*, which are optically active :

$$OR \cdot CH_2\ CH(OR') \ CH_2 \cdot O \cdot PO(OH) \cdot O \cdot CH_2 \cdot CH_2 \cdot N(CH_3)_3 \cdot OH,$$

where R and R′ are fatty acid residues.

Lecithins are found in the brain, yolks of eggs, and many seeds and are soluble in alcohol, and, to a less degree, in ether ; they give salts with acids and with bases and yield solid compounds with chloroplatinic acid or cadmium chloride. They are saponified by baryta, with formation of choline, fatty acids, and glycerophosphoric acid.

Of the *nitric esters* of glycerine, the most important is *trinitroglycerine*, or trinitroglyceric ester, $C_3H_5(ONO_2)_3$, which is one of the most powerful explosives. We shall hence study it from the industrial standpoint, first discussing certain general notions concerning explosives. The manufacture of the latter constitutes one of the most interesting industries of organic chemistry, partly because of the varied mechanical appliances which it requires.

EXPLOSIVE SUBSTANCES

The name explosive substances, or explosives, is given, in general, to those solid and liquid bodies which, under the influence of heat, percussion, electrical discharge, &c., are transformed instantaneously and completely—or nearly so—into a gaseous mass with an enormously increased temperature.

If the reaction takes place in a closed space, the gases thus produced and heated exert a very considerable pressure which can be immediately transformed into mechanical work, the enclosing substance and all the surrounding objects being shattered with great violence and noise. Such a phenomenon (or effect) constitutes a so-called *explosion*, and if it attains very great rapidity and power it is termed a *detonation*. For a constant quantity of gas produced in an explosion, the effect will be the greater the higher the temperature developed in the reaction.

THEORY OF EXPLOSIVES. The chemical reactions and physical phenomena of explosives are produced under conditions differing greatly from those in which physical and chemical properties of substances are usually studied. The pressures, temperatures, and velocities with which we have to deal in ordinary phenomena are of a very different order from that of the enormous pressures of the gases in the interior of the earth's crust, which are measured in hundreds of thousands or millions of atmospheres. So also the temperatures in various stars, *e.g.* in the sun, reach thousands of degrees, and the velocities of the planets hundreds of kilometres per second. The phenomena now to be considered, although they do not attain these enormous magnitudes, still do approach them. Indeed, explosions give pressures of tens of thousands of atmospheres, temperatures of thousands of degrees, and velocities (of projectiles) of thousands of metres per second.

Almost all explosive substances contain oxygen (furnished by chlorates, nitrates, &c.), only very few, such as nitrogen chloride and iodide, and aniline fulminate, being without it. Mixtures of oxidising agents with readily combustible substances (sulphur, carbon, sugar, &c.) are explosive, but they are less powerful than those composed of single compounds which explode by themselves. This is because the elements necessary for complete combustion are in much greater proximity, being present in the molecule of the explosive itself ; examples of such explosives are nitroglycerine, guncotton, mercury fulminate, picric acid, &c.

The determination of the *theoretical power* of an explosive requires a knowledge of : (*a*) the *chemical reaction* accompanying the explosion, so that the heat of the reaction, the temperature, and the volume and relative pressure of the gases formed can be deduced ; (*b*) the *velocity of the reaction*. In order to understand the theory of explosives, it is indispensable to call to mind the fundamental principles of thermochemistry and of thermodynamics, for which the reader is referred to the brief account given in vol. i, pp. 49 and 57.

(*a*) The *chemical reaction* is deduced from the difference in composition between the explosive and the products resulting from the explosion. When there is sufficient oxygen in the explosive to produce complete combustion, the nature and quantities of the gases can be calculated *a priori*, and from their heats of formation their temperature can be deduced. The total combustion of nitroglycerine, when exploded in a closed space, gives the following products (*a*): $2C_3H_5(NO_3)_3 = 6CO_2 + 5H_2O + 3N_2 + O$.

When there is deficiency of oxygen, as in guncotton and other substances, it is not easy to foretell the products of the reaction, as these vary with the conditions in which the explosion occurs, and usually several reactions take place simultaneously. Further the gases found after the explosion of such products are probably not always those formed at the instant of the explosion, as at such high temperatures certain substances (H_2O, CO_2, &c.) may undergo dissociation with absorption of heat.[1]

(*b*) *The heat developed in the explosion* is deduced by calculation from the thermochemical data of the equation, but the practical result is not in accord with the theoretical calculation, since part of the heat (25 to 30 per cent.) that should theoretically be developed is transformed into mechanical work, which is what is utilised in practice. In calculating theoretically the *heat of explosion*, the *heat of formation* of the explosive (from the elements) is subtracted from the heat that should theoretically be developed in the reaction. The heat of explosion varies, however, according as it is determined at *constant volume* or at *constant pressure*; in the latter case the explosion of nitroglycerine, for example, is effected in the open air, since then the volume varies, but the pressure is only that of the atmosphere.

The heat of formation of nitroglycerine from its elements (*see* p. 25) is given by the following equation (*b*): $C_3 + H_5 + N_3 + O_9 = C_3H_5(NO_3)_3 + 98$ Cals.

The heat of reaction of nitroglycerine can be calculated from equation (*a*) given above, from which it is seen that 2 mols. or 454 grms. of nitroglycerine yield $6CO_2 + 5H_2O + 3N_2 + O$. The heat of formation of $6CO_2$ is $6 \times 97 = 582$ Cals., and that of $5H_2O$, $5 \times 68{\cdot}5 = 342{\cdot}5$ Cals. For the nitrogen and oxygen there is no development of heat since they are not combined, so that the total heat of reaction calculated on the gases formed in the explosion of 2 grm.-mols. of nitroglycerine will be 924·5 (*i.e* 582 + 342 5) Cals. From this must be subtracted the heat of formation from the elements of 2 mols. of nitroglycerine, since on decomposing under these conditions of temperature the explosive first of all liberates its atoms, absorbing as much heat as is evolved in its formation from its elements (reaction *b*), *i.e.* 196 (98×2) Cals. per 2 mols. The atoms thus liberated combine immediately to give the gases which result from the explosion, the heat of formation of which has already been calculated.

The true theoretical heat of explosion at constant pressure for 454 grms. of nitroglycerine will hence be 728·5 (*i.e.* 924·5 − 196) Cals., or for a kilo, 1603 Cals. The heat of reaction at constant volume—the explosion occurring in a closed vessel—is rather higher, the heat corresponding with the expansion of the gas (*see* vol. i, pp. 26 and 50) not being absorbed as no expansion takes place; theoretically the heat at constant volume is calculated to be 1621 Cals. per kilo.[2] Serrau and Vieille, by direct practical measurements, found the heat of explosion of nitroglycerine at constant volume to be 1600 Cals., which confirms the accuracy of the calculation.

With substances which themselves contain sufficient oxygen for complete combustion

[1] The following Table gives the percentage compositions of the gases resulting from the normal explosion of various explosives in the calorimetric bomb:

	CO	CO_2	O_2	CH_4	H_2	N_2
Nitrocellulose powder	46 87	16 8	0 08	1·26	20 44	14 9
Gelatine dynamites	34 0	32 68	—	0 75	10 0	21 0
Carbonite	36 0	19 2	—	2 8	27 6	14 4
Picric acid	61 05	3·46	0 34	1·02	13 18	21 1
Trinitrotoluene	57 01	1·93	0 11	—	20 45	18 12

[2] For every gramme-molecule of a substance passing from the solid or liquid to the gaseous state, owing to the new volume occupied, 590 small calories (vol. i, pp 26 and 50) are absorbed. In the explosion of 2 mols of nitroglycerine, 14·5 mols of gas ($6CO_2 + 5H_2O + 3N_2 + O$) are formed, and these, on expanding, will absorb $14{\cdot}5 \times 590 = 8550$ small calories, or 8 5 Cals. per 454 grms of nitroglycerine, *i e* 18 Cals per kilo This, added to 1603, the heat of reaction at constant pressure, gives 1621 Cals as the heat of reaction at constant volume.

during explosion, it is not easy to calculate theoretically the heat of explosion, since the products of the reaction are not exactly known; in such cases, various direct practical determinations must be made.

It is not easy to calculate theoretically the *temperature of the gases* at the moment of explosion, since the specific heat of the gases at such high temperatures cannot be determined, but is certainly rather higher than the ordinary value. Further, at such temperatures dissociation phenomena occur which cannot be defined; these, however, lower the temperature, although not greatly, since with the great pressures developed the dissociation is minimal. On the other hand, with the means we possess, it is not possible to measure these temperatures directly and only approximately can they be determined for black powder. In general, however, they are very high and in some cases exceed 4000° (for instance, by burning ballistite in the air, platinum with m.pt. 1800° is easily melted), but even these temperatures, deduced indirectly, are much lower than those calculated theoretically.[1]

The *temperature of ignition* does not usually coincide with the temperature of explosion since explosion is caused not so much by the temperature as by the pressure and other factors to be considered later; so that for explosion to occur, special conditions (detonators) are necessary. But for some substances, *e.g.* black powder, non-compressed guncotton, &c., the temperature of ignition, given in the following Table, is identical or almost so with that of explosion:

Fulminate of mercury . . .	200°
Non-compressed guncotton	220° to 250°
Nitroglycerine	218° (explodes at 240° to 250°)
Black powder	288°

There are thus explosives which explode when merely ignited with a match and others which are exploded indirectly by means of detonators.

The *mechanical work*, in kilogram-metres, yielded by an explosive is calculated by multiplying the number of calories developed in the explosion of 1 kilo of the substance by the mechanical equivalent of heat (= 425, *see* vol. i, pp. 50 and 51). For various explosives this mechanical work (or *potential energy*) is given in the following Table:

Nitroglycerine .	(1 kilo) = 1600	Cals. × 425	= 680,000	kilogram-metres
Explosive gelatine .	= 1530	,,	= 650,000	,,
Dynamite	= 1178	,,	= 500,000	,,
Guncotton	= 1074	,,	= 456,000	,,
Fine sporting powder .	= 849	,,	= 360,000	,,
Potassium picrate	= 780	,,	= 330,000	,,
Fulminate of mercury	= 403	,,	= 170,000	,,
Nitrogen chloride . . .	= 339	,,	= 144,000	,,

Owing to various causes, the total theoretical energy of explosives cannot be utilised practically; *e.g.* the expansion of the gases at the moment the projectile leaves the cannon or gun, the friction, the heating of the barrel, &c., all constitute losses of the useful effect of the explosive.

The *volume of the gases* formed in the explosion can be calculated with reference to 0° and 760 mm., taking account of the fact that at the moment of explosion the water is in the state of vapour. But in practice it is of more importance to calculate the volume at the temperature of explosion, when a knowledge of the gases formed is possible, as is the case with nitroglycerine, and, in general, with explosives containing sufficient oxygen

[1] Indeed, water-vapour, formed from $H_2 + O$, should have theoretically a temperature of 7927° (*see* Calculation, vol. i, p. 378), but in the most favourable theoretical conditions the oxy-hydrogen flame does not exceed 2500°. For carbon dioxide the heat of formation is 97,000 cals., and the specific heat 0·217, so that for 44 grms. of CO_2 gas (grm.-mol.) the temperature attainable would be $\frac{97,000}{44 \times 0.217} = 10,160°$, and allowing for the fact that along with the 6 mols of CO_2 and 5 of H_2O, the 3 mols of N_2 and half a mol of oxygen formed in the explosion of nitroglycerine are also to be heated the theoretical temperature of the gases from the explosion would be about 7000°. This theoretical temperature is determined in general by the formula $t = \frac{C}{ps + p's' + p''s''}$, where p, p', p'' . . are the weights of the gases formed in the explosion, s, s', s'' . . their specific heats, and C the total heat in calories.

for their complete combustion. It is, however, not easy to calculate the volume of gas formed by products containing an insufficiency of oxygen, like guncotton, &c., with which the gases vary quantitatively and qualitatively according to the type of explosion ; in such cases the volume must be determined directly.

The volume of gases is calculated (*see* vol. i, p. 34) by means of the general formula,

$$V_t = \frac{V_o (1 + 0{\cdot}00367\, t)}{P}$$

where V_t is the required volume at the temperature of explosion t, V_o is the volume at 0° and 760 mm. pressure (which can be found from the weight of the gases formed), and 0·00367 is the coefficient of expansion for all gases. For such high temperatures and pressures, however, the coefficient of expansion is rather higher than that resulting from Gay-Lussac's and Boyle's laws, but this difference is compensated for by the somewhat higher specific heat of the gas at high temperatures, in consequence of which more than the theoretical quantity of heat is absorbed.

The *pressure of the gas* is deduced from the general formula given above, V_t being diminished by the volume v of the mineral, non-gasifiable residue (in the case of dynamite or other mixtures), so that :

$$P = \frac{V_o (1 + 0{\cdot}00367\, t)}{V_t - v} ;$$

with nitroglycerine, guncotton, &c., $v = 0$. P is the maximum theoretical force of an explosive, starting from its volume (solid) at the ordinary temperature, but the effect of a given explosive will be the greater as its density increases, that is, the greater the weight for the same volume ; and for guncotton, for example, the effect will be the greater for the same volume, the more it is compressed. Thus the relative specific gravities of different explosives are of importance, and in fact fulminate of mercury, which has a high specific gravity (five times that of ordinary powder and three times that of nitroglycerine), has a maximum rapidity of reaction and is the most powerful detonator, being capable of exerting a force of about 27,000 kilos per square centimetre (atmospheres), this being about treble that given by any other known explosive.

In practice, pressures higher than any imaginable may be attained when the volume occupied by a given weight of explosive in a closed vessel is less than the *critical volume of the gas* developed, since this critical volume (vol. i, p. 28) cannot be diminished by any pressure, however great. If we term *charging density* the ratio between the weight of the explosive in grammes and the volume in cubic centimetres occupied by it in absolutely filling its envelope (as though it were liquid or fused), this charging density corresponds with the specific gravity of the explosive ; if this density equals or exceeds the *reciprocal of the limiting volume* $\left(\frac{1}{v}\right)$ into which the gases developed (critical volume) can be compressed, the pressure attained will be infinitely great and will rupture any enclosing vessel, no matter how resistant it may be. The reciprocal of the critical volume of the gases produced in the explosion is termed the *critical specific volume* (or *limiting density*), and comparison of this with the *density of charge* leads to consequences of practical importance.

	Limiting density of the gases	Specific gravity of the explosive
Black powder	2·05	1·75
Nitroglycerine	1·40	1·60
Powdered guncotton	1·16	1·20
Picric acid	1·14	1·80
Fulminate of mercury	3·18	4·42

Thus, black powder has a charging density (or specific gravity) of 1·75 to 1 82, which does not reach the limiting density, so that even if it is exploded in its own volume it does not break the envelope if the latter is strong enough to withstand the pressure developed, namely, about 29,000 kilos per square centimetre. For granular powder, the density of which is 1, the pressure is only 6000 kilos. The real density (specific gravity) of compressed guncotton is 1·2, that of nitroglycerine 1·6, and that of picric acid 1·8, all of these being

superior to the limiting densities of the corresponding gases; so that when they explode in their own volume, all of these explosives burst the most resistant envelope, and, in such cases, the *velocity of the explosive wave* becomes infinitely great. Fulminate of mercury, although it has the high limiting density 3·18 (owing to the low critical volume, v), has a specific gravity of 4·42 (to which the density of charge approximates) and behaves like nitroglycerine, &c.

As it is difficult to calculate *a priori* the pressures exerted by explosives, it is preferable to determine them relatively by measuring certain effects of the gases at the instant of explosion; this is done, for instance, by observing the crushing or deformation of small cylinders of copper or lead, which are termed *crushers* (Fig. 179).

The total pressure depends on the character of the explosive and on the nature of the explosion (*see later*), but more especially on the density of charge.

The *specific pressure* of an explosive is a constant (a), given by the ratio of the pressure (p) to the corresponding density of charge (d) of the explosive itself: $a = \frac{p}{d}$. This specific pressure a is characteristic of any explosive and *expresses the pressure developed by unit weight* (1 grm.) *of an explosive in unit volume.* The specific pressure is not always the maximum pressure that can be exerted, this depending, as we have seen, on the charging density in its relation to the critical volume.

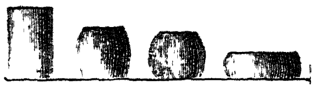


FIG. 179.

Velocity of reaction. The *duration of the explosion* is of great importance, since on it depends the greater or less utility of the explosive for different purposes. The more rapid the explosion the better is the heat developed utilised, so that this can be used almost entirely in heating and expanding the gases and so increasing the pressure considerably. If, however, the reaction is slow, a large portion of the heat is dissipated by radiation and conduction.

Explosives with an extremely rapid reaction produce special effects, as they shatter the envelope or rock in immediate contact with the explosive into minute fragments—an effect often not desired. These are termed *shattering* or *detonating explosives* and their properties are utilised in certain cases, as, for example, where a small cavity is to be made in a rock so that a large quantity of a *progressive explosive* may be subsequently introduced.

If the reaction, although rapid, is not instantaneous, the explosion produces other effects, for instance, the cleaving of large stones or rocks and the projection of fragments nearer to the explosive; this progressive or rending action is the effect usually desired by miners.

According as the gasification takes place more or less instantaneously (and the one or the other effect can be obtained with the same substance by adding inert materials to, say, dynamite, or mixing paraffin with guncotton), explosives are more or less shattering. Thus, panclastite is more shattering than guncotton, the latter more than dynamite, and this more than smokeless powder, which is a progressive explosive.

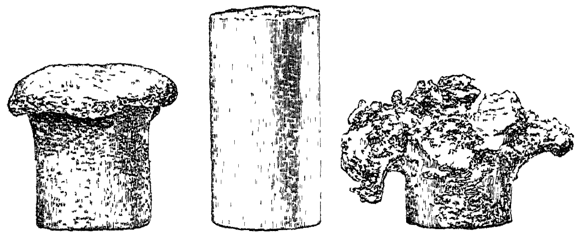
Many substances explode only with detonators (of fulminate of mercury) and the cause of the explosion in such cases is not only the high temperature produced by the explosion of the detonator, but more especially the great immediate pressure resulting from the instantaneous production of gas, this pressure and the sudden shock provoking the decomposition of the molecules of the explosive (Berthelot, Abel, Vieille). The *duration of explosion* or of gasification of the detonator is 500 times less than that of the explosive material, and the greater relative amount of heat developed in a certain time by detonators explains their greater shattering power compared with that of progressive explosives. The most highly shattering materials are: fulminate of mercury, panclastite, compressed guncotton, and nitroglycerine. The duration of reaction for detonators is only about $\frac{1}{1000}$ of a second, the extraordinary effect of these explosives being due to the enormous amount of energy developed (1600 Cals. for nitroglycerine) in this short time and in the small space containing them.[1]

[1] The *velocity of combustion* (or of *deflagration*) is sharply distinguished from the velocity of the explosive reaction and is made use of it in certain cases, *e.g.* in the throwing of projectiles (expansive and progressive action); The velocity of combustion of explosives depends on, and increases with increase of, the pressure at which they decompose. Another factor influencing the mode of combustion of explosives is the maximum velocity with which the pressure develops.

The *exponent of the power of the pressure,* which admits of passing from one value to the other in the increase

As has been already stated, the shattering effect of a substance is rendered evident by exploding a few grammes of it on a cylinder of metal (*crusher*) and the actions of different explosives are compared by means of these deformed and disfigured crushers. Fig. 180 *B* shows a leaden cylinder before the explosion, whilst *A* shows the same cylinder after 10 grms. of dynamite (a progressive explosive) have been exploded on it and *C* the result of the explosion of 10 grms. of panclastite (from nitrotoluene).

One and the same explosive substance may be made to give either a shattering or a progressive effect by varying the velocity of the reaction, this usually depending on the power of the *initial shock* which causes the explosion. The more powerful the initial shock the greater is the amount of kinetic energy transformed into heat and hence the higher the temperature developed; therefore, also, the greater is the pressure of the resultant gases and the more rapid and powerful the effect of the explosive. The effects vary considerably with the manner in which the explosion is induced; thus, if a flame is brought near to non-compressed guncotton, the latter burns rapidly but does not explode; whilst if it is compressed and subjected to the action of a cap (detonator) of fulminate of mercury, a real and very powerful explosion occurs; similar phenomena are observed with nitroglycerine and dynamite.[1]



A B C

Fig. 180

DETERMINATION OF THE EXPLOSION. In order to induce the explosive reaction of a substance, it is sufficient to bring it at a single point to a certain *initial decomposition temperature* (by percussion, detonation, &c.), the sharp decomposition at this point then producing a new shock which heats the neighbouring points to the decomposition temperature, and so on, the explosion being thus communicated to the whole mass by a true *explosive wave*, which is enormously more rapid than simple burning. From this will be understood the great importance of detonators, which do not serve merely for ignition; and the difference will also be apparent between an ordinary explosion by ignition and percussion and that induced by fulminate of mercury detonators.

When the phenomenon of explosion is studied more closely, it becomes evident that the gases produced at the point of ignition tend to expand and hence to diminish the pressure at that point and also the rapidity of explosion, but if this initial expansion is impeded the pressure and hence the velocity of decomposition increase rapidly. In practice miners obtain this effect by filling the cavity containing the explosive with a

of the pressure is called the *modulus of progressivity* and serves to characterise the various explosives. Thus, this modulus varies from 1 25 to 1 50 for black powders and from 1·86 to 1 87 for smokeless powders, whilst that of picric acid is 2 82 and that of *Favier's explosive* (12 per cent of dinitronaphthalene + 88 per cent of ammonium nitrate) 3 25 As will hence be seen, these last two explosives have the dangerous property of furnishing accidental superpressures, owing to undulatory phenomena which always accompany the combustion of substances inflammable with difficulty In smokeless powders, the moderate progressivity compared with the great power constitutes a valuable safeguard in their use in firearms; in this they are surpassed only by black powders, which are, however, much less powerful

[1] The *percussive force* (kinetic energy) of an explosive serves best to establish the *shattering power* and is calculated by C E Bichel by means of the formula $\frac{mv^2}{2}$, where m denotes the mass of the gases formed in the explosion, or the weight of the explosive, divided by 9 81 and v is the *velocity of detonation* (i e. the time elapsing from the beginning of the explosion to its completion throughout the whole mass) For 1 kilo of an *explosive gelatine* (92 per cent of nitroglycerine and 8 per cent. of collodion cotton) with the *charging density*, 1 63, Bichel gives a velocity of detonation of 7700 metres per second, so that the percussive force in absolute units will be $\frac{1 \times 7700^2}{9\ 81 \times 2}$ = 3,021,916 kilogram-metre-seconds; *for black powder* (with a charging density 1·04) exploded under the same conditions in a closed vessel with a detonating cap, the velocity of detonation is 300 metres per second, so that $\frac{1 \times 300^2}{9\ 81 \times 2}$ = 4587 kilogram-metre-seconds; for *kieselguhr dynamite* (75 per cent. nitroglycerine) the velocity of detonation is 6818, and hence the percussive force, 2,369,272 kilogram-metres per second; for a *gelatine-dynamite* (63·5 per cent. nitroglycerine, 1·5 per cent. collodion cotton, 27 per cent. sodium nitrate, 8 per cent. wood meal), with a charging density of 1 67, the velocity of detonation is 7000 and the percussive force 2,497,452; for *trinitrotoluene*, with a charging density of 1·55, the velocity was 7618, and the percussive force 2,957,896; *guncotton*, with a charging density of 1·25, had a velocity of 6383, the percussive force being 2,076,589; and *picric acid*, with a charging density of 1·55, gave the velocity of detonation 8183, and the percussive force 3,412,920 kilogram-metre-seconds.

tamping of earth or stone. The same end may also be attained by increasing considerably the mass of the explosive and the surface of ignition, and this explains why certain substances burn, without exploding, in small quantities (guncotton, nitroglycerine, &c.), or when the ignition is confined to a limited area, whilst a powerful explosion may occur when a large quantity of explosive is used or when it is surrounded by a source of considerable heat.

For shattering explosives (*e.g.* fulminate of mercury) no tamping is used, since the reaction is so rapid that the atmospheric pressure, that is, the air itself with its inertia, is sufficient to maintain the pressure of the gases. Even fulminate of mercury, if ignition is effected by an electric contact (which heats a platinum wire to redness) and under an evacuated bell-jar, burns without exploding, thus confirming the tamping action of the air in the case of detonators and even of ordinary explosives; in fact, if a roll of dynamite is exploded on a bridge, the latter is cut in two owing to the tamping action of the air.

The *explosive wave* produced in the explosion of gaseous mixtures and of liquids and solids is only slightly related to waves of sound. The latter is transmitted from crest to crest with but little kinetic energy, with a small excess of pressure and with a velocity depending only on the nature of the medium in which it is propagated and of equal magnitude for all kinds of vibrations. The explosive wave, on the contrary, propagates the chemical transformation through the mass of the explosive substance, communicating from point to point of the decomposing system an enormous amount of potential energy and a great excess of pressure. The sound-wave is propagated in a mixture of hydrogen and oxygen with a velocity of 514 metres per second at 0°, but the velocity of the explosive wave in the same mixture (exploded at a point) is 2841 metres.

With guncotton, the velocity of this wave varies from 3800 to 5400 metres per second according to the compression; with nitroglycerine it is 1300, with dynamite 2700, with picric acid 6500, and with nitromannitol 7700 metres per second. This velocity depends only on the nature of the explosive and not on the pressure, but it varies to some extent with the nature of the envelope. For instance, in a rubber tube having a thickness of 3·5 mm. and an internal diameter of 5 mm. and covered with cloth, ethyl nitrate gives a velocity of 1616 metres; whilst in glass tubes of various diameters and thicknesses the value is 1890 to 2480 metres. The propagation of the explosive wave bears no relation to that of ordinary combustion (which is much slower). The former occurs when the inflamed gaseous molecules acquire the maximum velocity or energy of translation, *i.e.* act with the whole of the heat developed in the chemical reaction.

Explosion by Influence. If a long row of dynamite cartridges are arranged on a flat solid at distances of 30 cm. or on a metal disc at a distance of 70 cm., explosion of the first with a fulminate cap results in the rapid and successive explosion of the remaining ones simply by influence and without the need of detonators or fuses. Air does not conduct the wave of explosive influence as well as solids, and if the cartridges are suspended in the air by wires such explosion by influence does not occur. Water conducts the explosive wave to a certain distance, but the influence gradually diminishes with increasing distance from the centre of explosion (there have been cases in which the shock of a large charge of guncotton has exploded neighbouring torpedoes; to avoid these inconveniences, so-called safety explosives are now used).

These explosive waves are first propagated through the explosive itself, not by a single shock—which would gradually weaken as it advanced—but by a very rapid series of such shocks produced by the propagation of the explosion from point to point of the whole mass of the explosive, the kinetic energy being thus regenerated along the whole course of the wave in the exploding substance.

An explosive wave is thus distinguished from an ordinary sound-wave by the fact that the latter becomes enfeebled as it advances, whilst the former is characterised by the uniformity of the energy transmitted from point to point by a series of numerous and successive explosions throughout the exploding mass. Only the last of these explosions is transmitted with its energy to the surrounding air and to the matter on which the explosive rests, and, since it is no longer reinforced (by other shocks), it weakens as it becomes more remote. Hence explosion by influence is not due to the fact that the distant explosive transmits or propagates the explosive wave through its own mass, but is owing to the arrest and transformation, at the point of impact, of the mechanical energy—it being capable

of similar (but not all) waves—into heat energy, able to cause decomposition and explosion of the substance itself.

The *effects* of large charges of dynamite (25 to 1000 kilos) when freely exploded are dangerous to buildings and to life for a distance of 500 metres and are felt as far away as 3 kilometres (L. Thomas, 1904).

CLASSIFICATION OF EXPLOSIVES. Explosives are to-day so numerous and are prepared from such different mixtures and serve such a variety of purposes that a rigorous or rational classification is difficult or impossible. Also with a large number of classes there would be many substances which might belong to more than one of them.

It will hence be preferable to limit ourselves to a description of the various explosives without any prearranged classification. They will be taken in the following order: (1) *Dynamites with a basis of nitroglycerine;* (2) *Nitrocellulose;* (3) *Various smokeless powders;* (4) *Picrate powders;* (5) *Explosives of the Sprengel type* (the components are explosive only when mixed); (6) *Sundry explosives;* (7) *Black nitrate and other powders;* (8) *Chlorate and Perchlorate powders.*

NITROGLYCERINES

This name is given improperly to nitric esters of glycerine since they do not contain true nitro-groups (NO_2) united directly with carbon as is often the case in benzene derivatives. On the contrary, the union is effected through an intermediate oxygen atom, so that these compounds should rather be called nitrates of glycerine.

Being a trihydric alcohol, glycerine can form three such compounds, the only one known until quite recently being trinitroglycerine containing 18·5 per cent. of nitrogen and having very considerable industrial importance.

In 1903, Mikolajczak prepared also pure DINITROGLYCERINE, $C_3H_5 \cdot OH(ONO_2)_2$, containing 15·4 per cent. of nitrogen, and he proposed to use it as an explosive, as it possesses almost all the ballistic advantages of trinitroglycerine and is not easily frozen; it is, however, very hygroscopic and readily soluble in water and in acids.

Dinitroglycerine is prepared by nitrating 100 parts of glycerine with 400 parts of nitric sulphuric mixture containing 8 to 12 per cent. H_2O, 60 to 70 per cent. H_2SO_4, and 15 to 32 per cent. HNO_3; at the end of the reaction, the mass is poured into an equal volume of water, and the acid neutralised with calcium carbonate, when the dinitroglycerine separates as a dense, floating oil. During the reaction, the temperature is maintained at 18° to 20° by cooling with ice. Dinitroglycerine is also formed by dissolving trinitroglycerine in sulphuric acid and then diluting the solution with a little water. In whatever way it is prepared (*e.g.* by treating 1 part of glycerine with 2 parts of sulphuric acid, separating by means of lime the glycerinedisulphuric acid formed and treating this with nitric acid, as proposed by Escales and Novak, 1906), a mixture of the two possible isomerides is always obtained: *dinitroglycerine K* (*i.e.* $\alpha\gamma$-), $NO_3 \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot NO_3$, and *dinitroglycerine F* (*i.e.* $\alpha\beta$-), $NO_3 \cdot CH_2 \cdot CH(NO_3) \cdot CH_2 \cdot OH$, which was studied by W. Will (1908). The mixture forms an almost colourless, faintly yellow oil, sp. gr. 1·47 at 15°, which freezes at below −30° to a glassy mass, this distilling almost undecomposed at 146° under reduced pressure (15 mm.); at 15° it is soluble to the extent of 8 per cent. in water and at 50° to the extent of 10 per cent. In dilute sulphuric or nitric acid it dissolves in all proportions and by sulphuric acid (up to 70 per cent.) it is transformed into *mononitroglycerine* and then into glycerine. It is very hygroscopic and, when dry, dissolves or gelatinises nitrocellulose (guncotton or collodion-cotton) very well. The two isomerides can be separated by taking advantage of the fact that, in the air, the *F* compound absorbs 3 per cent. of water and is transformed into a crystalline hydrate, $3(C_3H_6O_7N_2) + H_2O$, whilst the other remains liquid. The *F*-form gives a nitrobenzoyl-derivative melting at 81°, the corresponding compound of the *K*-isomeride melting at 94°. In the dry state, the dinitroglycerines are as useful for explosives as the trinitro-compound, but when moist they are much inferior. A mixture of 50 per cent. dinitro- and 50 per cent. trinitro-glycerine freezes below −20°.

Of MONONITROGLYCERINE, $C_3H_5(OH)_2 \cdot NO_3$, the pure α- and β-isomerides are known (W. Will, 1908). These are not true explosives and dissolve to the extent of 70 per cent. in water. The α-compound melts at 58° and boils at 155° to 160° under 15 mm. pressure.

Nitrochlorhydrin, $C_3H_5Cl(NO_3)_2$, and **Tetranitrodiglycerine** (*see* p. 184) have also been proposed as *non-congealing explosives*, but better still for this purpose are the nitroacetins (V. Vender) (*see later*).[1]

$$\text{TRINITROGLYCERINE,}\quad \begin{array}{l} CH_2O\cdot NO_2 \\ | \\ CHO\cdot NO_2 \\ | \\ CH_2O\cdot NO_2 \end{array} \quad \text{or } C_3H_5(O\cdot NO_2)_3.$$

This was discovered in 1846 by Ascanio Sobrero,[2] who called it **Pyroglycerine** and established its explosive properties but regarded its industrial manufacture as too dangerous. Its chemical composition was determined by Williamson in 1854. At first it was used only in small doses as a medicine, owing to its marked power of inducing dilatation of the blood-vessels. Later, after various unavailing attempts, Alfred Nobel succeeded in applying it industrially, and in 1863 established two nitroglycerine factories in Sweden, these rapidly prospering owing to the great demands of various nations for this powerful explosive. Nevertheless, owing to the neglect of precautions by consumers in the handling of nitroglycerine, various terrible explosions occurred which almost resulted in the abandonment and prohibition of this substance. Fortunately just at this time Nobel discovered a very happy solution of the problem which completely eliminated this danger, by mixing the nitroglycerine with inert substances (*kieselguhr* or *infusorial earth*) and thus obtaining *dynamite*, this being to-day at the head of the great explosives industry.

PROPERTIES. When pure it is a dense almost colourless or faintly yellow liquid of sp. gr. 1·6 at 15°, and when it freezes its density increases by almost one-tenth. It is odourless and has a sweetish, burning taste. It is almost insoluble in water (0·16 to 0·20 per cent. being dissolved at 15°), is not hygroscopic, and dissolves easily in concentrated alcohol, ether, benzene, chloroform, glacial acetic acid, toluene, nitrobenzene, acetone, olive oil, and concentrated sulphuric acid, and to a less extent in nitric acid and still less in hydrochloric acid; it is, however, insoluble in carbon disulphide, glycerine, petroleum, vaseline, turpentine, benzine, and carbon tetrachloride. In solution it will not explode. It evaporates spontaneously and in very small quantities even at 50°, and if gradually heated to 109° it begins to decompose with evolution of brown nitrous vapours.

Its specific heat is 0·356, and its heat of solidification 23 to 24 Cals.

[1] **Dinitromonochlorhydrin** is obtained, according to F. Roewer (1906), by nitrating the monochlorhydrin in the same manner as glycerine is nitrated (*see later*), and is then quickly separated from the top of the nitric-sulphuric acid mixture as an oil which is easily rendered stable by washing with water and soda. It forms a faintly yellow, mobile oil of aromatic odour, sp. gr. 1·541 at 15°, soluble in alcohol, ether, acetone, or chloroform, but insoluble in water and in acids. At 180° it gives yellow vapours, and at 190° boils without detonation or deflagration, and with only slight decomposition; under a pressure of 15 mm. it distils unchanged at 121° to 123° as an almost colourless oil. It is much more stable towards pressure than nitroglycerine, although possessing almost the same explosive properties. It does not freeze even at −30° and is not hygroscopic. It dissolves nitrocellulose, forming explosive gelatine, and mixes readily with nitroglycerine, giving non-congealing dynamites (with 5 to 20 per cent. of nitrochlorhydrin, Ger. Pat. 183,400), these being prepared by nitrating directly a mixture of glycerine and chlorhydrin. In order to avoid the inconvenient effects on miners of the hydrochloric acid formed in the explosion of nitrochlorhydrin, potassium nitrate is added; during the explosion this is transformed into potassium carbonate, which neutralises the acid.

Dinitroacetylglycerine, $C_3H_5(ONO_2)_2(OCOCH_3)$, is obtained by nitrating the monoacetin in the same apparatus as is used for nitroglycerine, but using an acid mixture containing a preponderance of nitric acid, *e.g.* 65 per cent. HNO_3 and 35 per cent. H_2SO_4. The dinitroacetylglycerine being somewhat soluble in water, it is lost to some extent during the washing. It is a yellowish oil, sp. gr. 1·45 at 15°, and is soluble in alcohol, acetone, ether, nitroglycerine, or nitric acid, and almost or quite insoluble in water, benzene, or carbon disulphide. It contains 12·5 per cent. of nitrogen and with double its weight of nitroglycerine gives a mixture with 16·5 per cent. of nitrogen, which has a lower freezing-point (below −20°) than any other mixture of these substances. It serves well for preparing non-congealing dynamites, and as it dissolves nitrocellulose easily it can be used for gelatinising smokeless powders.

Dinitroformylglycerine, $C_3H_5(ONO_2)_2(O\cdot CHO)$, is prepared in a similar manner to the preceding compound, or, together with nitroglycerine, by nitrating the product obtained by heating 2 parts of glycerine with 1 part of oxalic acid for 20 hours at 140°. Nitroformin and nitroacetin have explosive powers rather inferior to that of nitroglycerine.

[2] Ascanio Sobrero was born at Casalmonferrato on October 12, 1812. He first studied medicine and then chemistry. In 1840 he went to complete his chemical studies in the laboratory of the celebrated Pelouze at Paris, where he stayed two years, and in 1843 he worked in Liebig's laboratory at Giessen. In 1845 he became Professor of Applied Chemistry at Turin, where he taught until 1883. He died on May 26, 1888, after a modest life, during which he filled various honorary social positions. It was always his aim that science should not be made a pretext or means of dishonourable undertakings or of business speculations.

At a red heat it evaporates without decomposing, but if it begins to boil vigorously during the heating, there is danger of explosion. According to Champion, pure nitroglycerine in small quantities boils, giving yellow vapours, at 185°, evaporates slowly at 194°, and rapidly at 200°, burns quickly at 218° and detonates with difficulty at 241°, violently at 257°, feebly at 267°, and feebly with flame at 287° (being in the spheroidal state).

When heated in small quantities in the Bunsen flame, it burns without exploding, and if spread in a thin layer on paper it ignites with difficulty and burns only partially. Explosion of nitroglycerine can be induced either by violent percussion at a temperature of 250°, or by energetic detonation (*e.g.* by explosion of fulminate of mercury).

Nitroglycerine may be easily supercooled below its solidifying point. Kast (1906) showed that nitroglycerine represents a case of monotropic allotropy (*see also* vol. i, p. 191), *i.e.* it has two freezing-points, + 12° and + 13·5°, corresponding with different crystalline forms.[1]

When frozen, nitroglycerine explodes with more difficulty than in the liquid form. Pure nitroglycerine will not redden blue litmus paper or turn starch paste and potassium iodide blue, unless it contains free acids or nitrous compounds due to partial decomposition.

Impure nitroglycerine readily decomposes and may explode spontaneously, whilst in the pure state it keeps indefinitely. A sample of nitroglycerine (200 grms.) prepared by Sobrero in 1847 is still kept under water in the Nobel factory at Avigliana.

When decomposing, nitroglycerine turns green owing to the formation of N_2O and N_2O_3; CO_2, CO, H_2O, N, and O (*see also* p. 216) are also successively formed. In exploding, 1 litre of nitroglycerine produces 1298 litres of gas, which, at the temperature of explosion, occupies a space of 10,400 litres.

In large doses nitroglycerine is poisonous and its vapour causes headache (especially at the back of the head), giddiness, and vomiting. These effects are produced even by working with or simply touching nitroglycerine and are cured by means of cold compresses on the head, by breathing fresh, pure air, and by drinking coffee and taking suitable doses of morphine acetate.

Workmen who handle the nitroglycerine paste during the manufacture of the various dynamites become habituated to it in two or three days and afterwards feel no ill-effects. Nitroglycerine is moderately easily decomposed by alcoholic potassium hydroxide (with separation of glycerine), and, when necessary, this reaction is employed to destroy and render harmless small quantities of nitroglycerine; similarly benches or floors on which nitroglycerine is spilt are washed with caustic alkali solutions:

$$C_3H_5(ONO_2)_3 + 5KOH = KNO_3 + 2KNO_2 + CH_3{\cdot}COOK + H{\cdot}COOK + 3H_2O\,;$$

a little ammonia is also formed. With reducing agents it gives ammonia and glycerine, whilst with concentrated sulphuric acid it yields nitric acid and glycerinsulphuric acid.

[1] Both nitroglycerine and dynamites and smokeless powders prepared from it are liable to solidify, and although they are then more stable the thawing is accompanied by danger, and when not carried out with great precautions has often led to fatal explosions, these being sometimes caused by the mere rubbing of the crystals. Indications will be given later of the precautions taken in magazines to prevent freezing, and mention may be made here of the attempts which have been made to render *nitroglycerine non-congealable.* As early as 1895 it was proposed to add nitrobenzene to nitroglycerine to lower the freezing-point, and later the use of orthonitrotoluene was suggested, but the practical results were not very satisfactory in either case, the depression of the freezing-point being very small. Substances were required which were almost as explosive as trinitroglycerine, and were insoluble in water and stable on heating, and, in addition, were good solvents for nitrocelluloses (for making smokeless powders). These conditions were well satisfied by the *nitroformins* and *nitroacetins* tested by Nobel as early as 1875 but rendered practically useful in 1906 by V. Vender. The best results are given by *dinitromonoacetin* which is obtained from the *monoacetin* of glycerine prepared by the ordinary method used for esterifying alcohols with acids (*see later*, Esters) Forty parts of the monoacetin are introduced slowly into a mixture of 100 parts of nitric acid (sp. gr. 1·530) and 25 parts of oleum or Nordhausen sulphuric acid (containing 25 per cent. of free SO_3, *see* vol. i, p. 275), the mass being cooled so that the temperature does not exceed 25°. The whole is then poured into water and washed with cold and afterwards with hot (70°) dilute soda. By this means an oil is obtained having sp. gr. 1·45 and containing 12·5 per cent. of nitrogen; it is insoluble in water, carbon disulphide or benzene, but dissolves unchanged in nitric acid, nitroglycerine, methyl or ethyl alcohol, acetone, acetins, &c. Even in the cold, it has considerable solvent and gelatinising power for collodion-cotton and guncotton (with 13·4 per cent. of nitrogen) and the resulting explosive gelatines do not freeze even at −20°. Naukhoff (1908) has proposed the addition of nitromethane or nitroethane to dynamite to lower its freezing-point, and at the present time *liquid dinitrotoluene* is largely used for the same purpose.

Characteristic Reactions. According to Weber, small quantities of nitroglycerine are detected by treatment with aniline and concentrated sulphuric acid: a reddish purple coloration is obtained which turns green on addition of water. To establish the *purity* and keeping qualities of nitroglycerine, the nitrogen is determined and Abel's heat test carried out (*see later*, Testing of Explosives); if it is satisfactory, 2 c.c. of it withstands 20 to 30 minutes' heating at 82° without giving sufficient nitrous vapours to be detectable by means of starch and potassium iodide paper.

This reaction is, however, given by nitroglycerine kept for a few days at a temperature exceeding 45°, or for a long time below this temperature.

PREPARATION. It is obtained by the action of a mixture of nitric and sulphuric acids on glycerine:

$$C_3H_5(OH)_3 + 3HNO_3 = 3H_2O + C_3H_5(NO_3)_3.$$

The mono- and dinitro-compounds are probably formed as intermediate products of this reaction.

The presence of sulphuric acid, which plays no apparent part in the change, is usually regarded as being necessary to maintain the nitric acid at a high concentration, *i.e* to decompose the hydrates formed by nitric acid with the water from the reaction (HNO_3, H_2O—HNO_3, $3H_2O$) and so regenerate monohydrated nitric acid, which acts on the glycerine (Kullgren, 1908). If the function of the sulphuric acid were merely to fix the water, phosphoric acid could be used in its place: but if this is done no nitroglycerine is obtained.

The excess of the nitric-sulphuric mixture which is always used helps to produce a moderately complete separation of the nitroglycerine, which has a slightly lower density, so that it is possible to recover the acids employed. Although nitroglycerine is soluble in sulphuric or nitric acid alone, it does not dissolve in the mixed acids. But if one of the two acids is in large excess, a considerable amount of nitroglycerine remains in solution and is lost. In the nitration, the whole of the glycerine cannot be added at one time, since sufficient heat would in that way be developed to produce decomposition and explosion of the nitroglycerine instantaneously formed. It is also not convenient to reverse the operation, that is, to add the mixed acids gradually to the glycerine, the greater density of the latter rendering rapid and homogeneous mixing difficult; it is hence preferable to run the glycerine slowly into the acid mixture and to keep the latter continually and thoroughly stirred and cooled.

MANUFACTURE. The theoretical proportions of the reacting substances [1] would be 100 parts by weight of glycerine and 205·43 of pure nitric acid, the theoretical yield of trinitroglycerine being then 246·74 parts. But on a large scale the whole of the nitric acid does not come into immediate contact with the whole of the glycerine, and it is hence better to use a slight excess of nitric acid (240 parts or even more); the amount of sulphuric acid employed always exceeds that of the nitric acid (about $1\frac{1}{2}$ times). In modern factories the following proportions are often used: 100 kilos of glycerine, 240 to 260 kilos of nitric acid (98 per cent.), and 340 to 360 kilos of sulphuric acid (96 to 98 per cent.).

In the best factories, the *practical yield* is 215 to 232 kilos of nitroglycerine per 100 of glycerine, but in some cases it amounts to only 205 to 210 kilos. Good yields are obtained by cooling the acid mixture during nitration by means of solutions from cooling machines, the temperature of reaction being kept down to about 10°.

The low value of the practical compared with the *theoretical yield* (246·7) is due to the fact that towards the end of the reaction there is very little free nitric acid and the last

[1] The prime materials used in the manufacture of trinitroglycerine should be subjected to rigorous control; the *glycerine* should be pure and distilled and should satisfy the requirements indicated on p. 188. The *nitric acid* should have a specific gravity of 1·500 (48° Bé. or about 95 per cent HNO_3) and should not contain more than 1 per cent. of nitrous acid, *i.e.* it should not be yellow, as otherwise an increased amount of heat is evolved during nitration and the yield is lowered. The *sulphuric acid* should be pure, with a sp. gr. of 1·8405 (*i.e* at least 96 per cent. H_2SO_4) and acid containing more than 0·1 per cent. of arsenic should be avoided; lead and iron should also be absent as they might lead to reduction. When nitrations are carried out with nitric-sulphuric acids almost free from water (1 to 2 per cent.) the sulphuric acid is replaced by *oleum* or Nordhausen acid (*see* vol. i, p. 275), *i.e.* acid containing 20 per cent. or more of dissolved sulphur trioxide.

portions of glycerine added are nitrated only with difficulty and hence remain dissolved in the sulphuric acid.

The mixture of nitric and sulphuric acids, which is prepared separately, is made by pouring the sulphuric acid slowly into the nitric acid (not *vice versa*) in an iron vessel, the mixture being kept well cooled and stirred. With this procedure there is no danger of the acid spurting, and no production of nitrous fumes, since the development of heat is gradual. This mixture is forced by means of elevators (*Montejus*) or pulsometers working with compressed air (vol. i, p. 264) into tanks which feed the leaden apparatus in which the glycerine is nitrated.

During recent years, many vitriol and explosives works have made considerable use of Kuhlmann emulsors (or *Mammoth pumps*) for raising concentrated acids, which are rendered lighter by emulsification with air (*see illustration*, vol. i, p. 265).

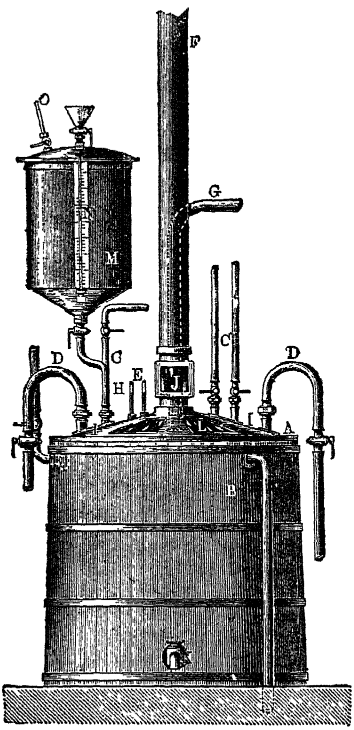


FIG. 181.

The leaden nitration apparatus is shown in Fig. 181. It is surrounded by a wooden jacket inside which water circulates. Inside the vessel are peripheral leaden coils through which large quantities of cold water are continually passed by means of the two tubes *D*. The tubes *C* lead dry compressed air to the bottom of the liquid, which is thus kept thoroughly mixed. The tube *F* serves as exit for the air, and for any nitrous vapours which may be evolved and may be observed through the window, *I*; these vapours are recovered in small condensation towers sprinkled with a little water. The cold acid mixture is first introduced through the pipe *G*. The glycerine, at a temperature of 20° to 25° (if colder it would be too viscous), is measured in the reservoir, *M*, and is passed, by means of compressed air supplied through *O*, slowly into the tube *H*, and thence into a perforated circular pipe at the bottom of the apparatus. Two thermometers, *E*, show the temperature of the reacting mass at any moment.

The bottom of the apparatus is slightly inclined and at the lowest part is inserted a large stoneware tap, *K*, with an ebonite screw containing an aperture of at least 5 cm. It is convenient to have two of these taps so that, in case of danger, the whole of the mass may be rapidly discharged into a vessel of water underneath (*drowning* of the nitroglycerine). In such an apparatus, the same quantity of nitroglycerine is produced each time and the treatment of 100 kilos of glycerine requires less than half an hour.[1] In America as much as 2000 kilos of glycerine are worked at one time in open vessels provided with stirrers, but the risk, in case of explosion, is greatly increased. At the conclusion of the operation the nitroglycerine (sp. gr. 1·6) floats on the acids (sp. gr. 1·7) and is separated by means of a suitable decanting apparatus (Fig. 182) to the bottom of which the whole mass is passed through the tube *K*. The apparatus consists of a leaden tank with its base sloping towards

[1] The temperature during the reaction should not exceed 25° to 30°, and it can be regulated by passing the cooling water more or less rapidly through the coils, and, if necessary, through the wooden jacket; increase of the air-current also helps to lower the temperature. Rise of temperature and consequent explosion were at one time due principally to the use of impure glycerine, but nowadays it is generally due to slight escape of water from the coils. In order to avoid such danger, the apparatus and coils are tested at least once a day, usually in the evening when the plant is free; water under pressure is forced into the coils and jacket and left until the morning, when any leak can be detected. Although the apparatus is constructed of very thick plates, the lead corrodes in time; tests made with aluminium apparatus (proposed by Guttler) have not been very successful. Some works now employ more solid vessels of wrought or cast iron, which are more easily cooled

Boutmy and Faucher avoid the dangers of violent reactions by first dissolving, *e.g.* 100 parts of glycerine in 320 of sulphuric acid and then pouring the solution into a mixture of 280 parts of nitric and 280 of sulphuric acid. After 12 hours the reaction is complete, the yield being 190 per cent., calculated on the weight of the glycerine taken. This method did not give good results in England, but has been applied in France

Kurtz increases the yield and accelerates the reaction by emulsifying the glycerine with air and passing it under the acid mixture, a more intimate mixture being thus obtained.

the centre and supported by a wooden structure; the cover, C, is raised on wooden joists, B. The tube D, with the glass window, E, serves to carry off any gas which may be evolved; a thermometer is inserted into the vessel at t. The tube shown at the bottom and in the centre of the apparatus communicates with two or three taps, H, and is also fitted with a window, F.

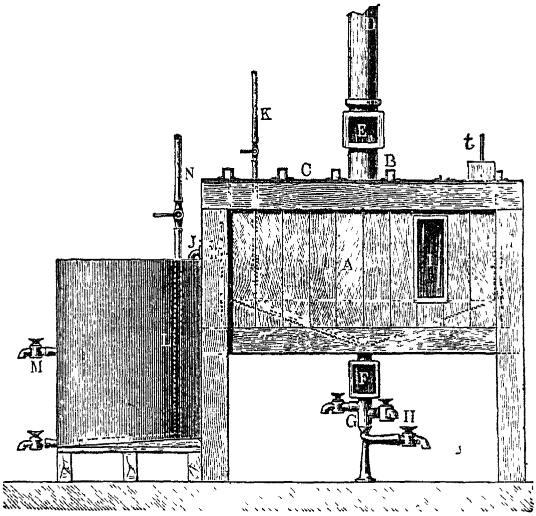


FIG. 182.

After half an hour, the nitroglycerine in this vessel separates into a distinct layer, as may be seen through I. The surface of separation of the two layers coincides very nearly with the tap J, so that the nitroglycerine can be discharged almost completely through the tube J into the lead-lined wooden tank, L. The acid that remains is discharged through one of the taps, H, it being noted through F when a turbid layer appears, as this separates the acid from the nitroglycerine and contains various nitro-products and certain impurities.[1]

The tap, H, is then closed and this liquid is passed through other taps into suitable washing and decanting vessels (*see later*). The nitroglycerine in L is washed with water

[1] The acid separated from the nitroglycerine and containing about 72 per cent H_2SO_4, 9 per cent HNO_3, 16 per cent H_2O, and 3 per cent of dissolved nitroglycerine, is collected in leaden tanks in which it remains for one or two days, during which time a small quantity (about 0.5 per cent) of nitroglycerine separates at the surface. The dangers of this *slow separation* are sometimes avoided by neglecting the nitroglycerine which separates after 4 to 5 hours, to avoid danger in succeeding nitrating operations, a large proportion of the nitroglycerine remaining dissolved is decomposed by adding cautiously 4 to 5 per cent of water so as to raise the temperature to 35° to 40° and then again mixing the mass by means of air (part of the trinitroglycerine is thus transformed into soluble dinitroglycerine). These recovered acids, which are utilised again, are first denitrated in the apparatus shown in Fig. 183. This consists of a cylinder of earthenware or volvic stone filled with fragments of silica (quartz) or glass, on to which the acid from the tank, D, is sprayed; a current of steam from the cock, a, together with a little air are passed upwards through the tower. As the temperature rises the organic matters are oxidised at the expense of the nitric acid, which thus gives oxide of nitrogen, this passing with the other nitrous vapours into the tube, H, which is supplied with a current of air from the injector, H. The mixed vapours are divided between a double battery of long vertical earthenware pipes, G, where nitric acid of 38° to 40° Bé. condenses, any vapour escaping being finally condensed in a Lunge-Rohrmann tower.

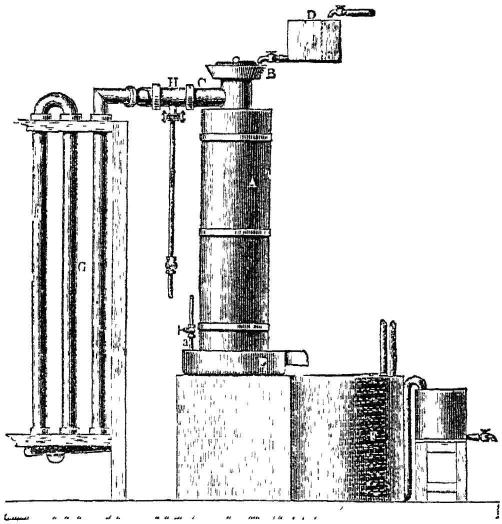


FIG. 183.

The sulphuric acid at last reaches the bottom of the tower, A, where it collects in the basin, E, and thence passes through the leaden cooling coil, F. The acid thus obtained is darkened by the impurities present and has a density of about 56° to 58° Bé; it is usually concentrated in cascade apparatus of the Negrier type or in Gaillard towers (*see* vol. i, p. 269).

During recent years, instead of the sulphuric and nitric acids being recovered and concentrated separately, it has been found preferable to send the acid mixture—after decomposition of the dissolved nitroglycerine (*see above*)—directly but carefully into the boilers (already containing the sodium nitrate) in which nitric acid is made. Some prefer to *revivify* the acid mixture, *i.e.* to bring it up to its original strength by adding the necessary quantities of fuming nitric and sulphuric acids, so that it can be used again for the production of fresh quantities of nitroglycerine; for this purpose, sulphuric acid or oleum is added slowly to the required amount of concentrated nitric acid and the mixture then poured into the weak acid. For this process of recovering the weak acids (by which the 2.5 per cent or so of nitroglycerine dissolved in the acid is recovered) to be employed, a cheap supply of sulphuric anhydride or oleum must be available (oleum at less than 4*s.* per quintal).

and is then agitated by passing compressed air through the perforated pipe, *N*, for about fifteen minutes ; the nitroglycerine is allowed to settle and the water decanted off by means of the upper tap, *M*. The washing with water is repeated two or three times, all the washing water being collected in a single tank [1] Finally the nitroglycerine is passed into a similar vat where it is *stabilised*, *i.e.* washed alternately with very dilute soda solution and water until the wash-water no longer has an acid reaction towards litmus and the nitroglycerine has a feeble alkaline reaction (0·01 of alkalinity, which disappears later).

In the British Government factory at Waltham Abbey, Nathan, Thomson, and Rintoul (Eng. Pats. 15,983, 1901 ; and 3020, 1903) prepare nitroglycerine in large leaden vessels (*a*, Fig. 184) with inclined bottoms ; in these 300 to 500 kilos of glycerine are treated at one time and at the end of the operation, after 50 to 60 minutes' rest, the acid recovered from a preceding operation is passed from the tank, *c*, to the bottom of *a*. In this way the nitroglycerine is displaced and caused to discharge through *s* into the washing vessel, *e*, exit for the vapours being supplied by the tube *o*. When all the nitroglycerine has been forced out, a little of the acid mixture is drawn off by the pipe *i*, 2 to 3 per cent. of water being then slowly added to the remainder, which is mixed meanwhile with a current of air. By this means the dissolved nitroglycerine is decomposed and the dangers of slow separation in any of the vessels avoided (*see* preceding Note). The acid is immediately denitrated, after sufficient has been passed into the tank, *c*, to displace the nitroglycerine of the succeeding operation. *b* is the tank in which fresh acid is mixed, *f* the vessel for drowning, *g* that for stabilising, and *h* the filter for the nitroglycerine, these two being at a considerable distance from *e* so that the nitroglycerine may be conducted to them as soon as it has undergone its initial rough washing. Yields of as much as 230 per cent. are obtained with this Nathan-Thomson process. In Italy it is used at the Villafranca (Tuscany) dynamite factory.

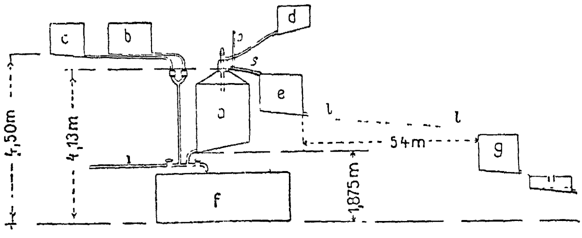


FIG. 184.

FILTRATION. The washed nitroglycerine is carried in hardened rubber or ebonite buckets to the filters, which are merely wooden frames covered with woollen cloth or felt to retain the impurities, scum, gummy matters, &c. By covering these cloths with a layer of dried salt, the emulsified water can also be held back. The cloths rapidly become blocked and are frequently renewed. The filtration is often, especially in England, effected by means of the apparatus shown in Fig. 185. This consists of a lead-lined tank, *A*, with inclined base. In the lid is inserted a leaden cylinder, *G*, with a metal gauze bottom on which rests a filtering cloth, *N*, and on this a layer of sodium chloride, *O*, covered by another filtering cloth kept stretched by a leaden ring, *Q* ; the free part of this cloth is folded, stretched, and fixed by a conical leaden weight, *R*. In place of salt, a sponge may be employed to retain the water. In some cases complete separation of the water from nitroglycerine is obtained by leaving the latter at rest for a couple of days in a tepid place (30°) and then decanting it ; but there

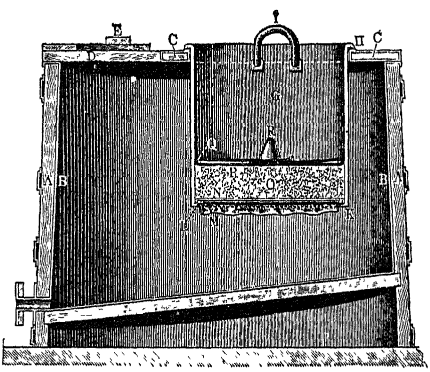


FIG. 185.

[1] The *wash-waters* from all the preceding operations are collected in an inclined lead-lined tank called the labyrinth, which is divided into a number of chambers by vertical leaden walls perforated alternately at the top and bottom. The wash-waters enter slowly at one end of the tank and traverse a long up-and-down course, gradually depositing the emulsified or suspended drops of nitroglycerine before the opposite end of the tank is reached. The nitroglycerine collected at the bottom is discharged through suitable taps and added to that in the washing apparatus.

is then some risk owing to the prolonged accumulation of large quantities of nitroglycerine.

In the working of nitroglycerine, each operation is usually carried out in a separate building, that in which the explosive is produced being at a very high elevation, the nitroglycerine then flowing to lower points for the succeeding operations. All these buildings are of wood so as to diminish the damage in case of explosion. The floors of the sheds in which the nitroglycerine is produced and of those where it is treated in the liquid state are covered with sheet-lead with raised edges so that the material may be caught in case of breakage.

Where the nitroglycerine is worked in a pasty state (for dynamites) the flooring is of wood free from crevices.

If nitroglycerine is accidentally spilled, it should be immediately wiped up with sponges.

The channels through which nitroglycerine passes from one shed to another are in the form of gutters furnished with removable covers and are fitted with a longitudinal pipe through which warm water can be circulated in winter and the danger of freezing avoided. A disadvantage attending the use of these channels is that an explosion in one shed is propagated along the channels to all the other sheds. So that the precaution is taken of disconnecting one section of a channel when not in actual use. In many factories the nitroglycerine is transported in rubber pails (*see above*).

The windows of the sheds are smeared with whitening, as the presence of curved parts in the naked glass might possibly result in the focusing of light on the explosive material and the explosion of the latter.

USES OF NITROGLYCERINE. Small quantities are sometimes used in medicine to induce dilatation of the blood-vessels, but practically the whole of the production is used as an explosive. In America it has been long in use in the pure state for large mining operations ; Mowbray freezes it and transports it in large quantities on trains from the factory to the place of consumption, as he regards it as less sensitive in the frozen state ; but this view is generally contested. It has also been transported without danger in solution in methyl or ethyl alcohol, from which it is reprecipitated with water at its destination. Almost all the nitroglycerine made is used in the manufacture of various kinds of dynamites, dynamite gelatines, explosive gelatines, smokeless powder, &c.

DYNAMITES. This generic name is given to explosives obtained by gelatinising or absorbing nitroglycerine by various other substances. We have already mentioned that Alfred Nobel, the father of dynamite, had from 1860 to 1864 various explosions of nitroglycerine, sometimes of that recovered from the alcohol in which it had been transported (*see above*). In his attempts to diminish the dangers of nitroglycerine by diluting it with inert substances, Nobel discovered in 1866 that it is absorbed by *kieselguhr* (*infusorial earth*) in considerable proportions (up to 81 per cent.), and that in this state its power is diminished but little, while it can be safely handled and transported. He found further that this *dynamite* is exploded only by means of a fulminate of mercury cap.

Kieselguhr is found in a very pure state in the Lüneburg moors, near Unterlüss in Hanover, and in an inferior quality in Scotland, Norway, and Italy. It consists almost exclusively of the siliceous remains of diatoms, and contains also traces of iron and organic matter. Its particles are formed of empty tubes perforated in all directions, and it is this structure which renders kieselguhr so highly absorbent. Under the microscope, it presents the appearance shown in Fig. 186. At the present time kieselguhr dynamite has been almost entirely replaced by new types (gums or gelatines) described later.

If the absorbing substances are inert, like infusorial silica (kieselguhr), sawdust, cellulose, &c., they form *dynamites with inactive absorbents*, which contain about 72 to 75 per cent. of nitroglycerine, 24·5 per cent. of kieselguhr, and 0·5 per cent. of soda for the No. 1 quality, and less nitroglycerine in the Nos. 2 and 3 qualities.

But in the new type of dynamite the solid matter consists of active substances, *e.g.* nitrocellulose, which take part in the explosion. These are *dynamites with active absorbents*,

the absorbents or bases being again divided into *nitrates* or *inorganic oxidising bases* and *organic nitro-absorbents* (collodion-cotton, &c.).

I. MANUFACTURE OF DYNAMITE WITH INACTIVE ABSORBENTS. The kieselguhr used must be suitably prepared. It is first spread out in furnace chambers

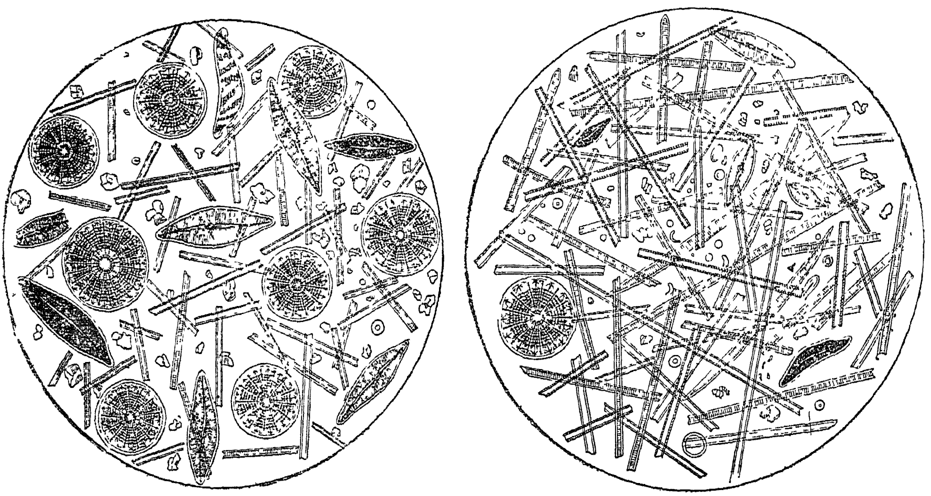


FIG. 186.

and gently heated to eliminate moisture and organic matter, and is then more strongly calcined in reverberatory or muffle-furnaces, excessive heating being avoided as it may destroy the absorbing properties. It is then ground into fine powder and sieved. The flour thus obtained should not contain more than 1 per cent. of moisture and should be immediately filled into sacks and consumed the same day, as otherwise it might absorb moisture. It consists of silica with traces of oxides of iron and aluminium.

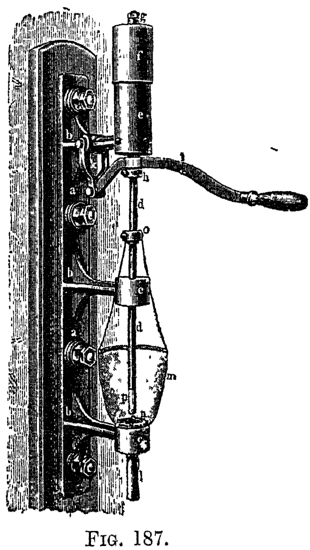


FIG. 187.

The nitroglycerine is weighed in buckets of hard gutta-percha or lacquered compressed wood-pulp and is carefully taken to the *mixing-house*, where it is poured into wooden troughs lined with sheet-lead, and containing the absorbent Skilled workmen then mix the mass rapidly by hand ; sometimes rubber gloves are worn, but usually the men prefer to do without gloves, as the hands become accustomed to the action of the nitroglycerine in two or three days.

It is important to obtain a homogeneous mixture, so that not the least portion of the kieselguhr remains free from nitroglycerine. After this hand-mixing the mass is rubbed through brass-wire sieves (2 to 3 meshes per centimetre) arranged above lead-lined wooden troughs. The dynamite is placed on the sieve with a wooden spatula and pressed through with the palm of the hand ; here, too, the use of rubber gloves is not popular with the operatives In the troughs the dynamite is in the form of fine grains, which should not be too dry or too *greasy*. If too dry, it is passed again through the sieve or mixed with more nitroglycerine, whilst if too greasy it is mixed with a further amount of kieselguhr. It is then placed in small portions in indiarubber bags or in wooden boxes lined with sheet-zinc and is removed to the building where the cartridges, used especially in mines, are prepared. Here the dynamite is transformed by simple presses into rolls, 19, 23, or 26 mm. in diameter. A very simple press devised by O. Guttmann is shown in Fig. 187. The dynamite is introduced into the cloth bag, *m*, and falls into the tube, *l*, being pressed into this by the lignum vitæ or ivory piston, *p*, at the end of the bar, *d*, which is actuated by the

lever, *i* ; the cylinder of dynamite issuing from the bottom of the tube, *l*, is broken by hand into definite lengths, which are wrapped in parchment paper or paraffined paper. The ordinary length is 10 cm (discharge cartridges) or 2·5 to 5 cm. (primers). These cartridge machines are sometimes worked by pulleys and motors. In some cases the *boudineuses* illustrated later are used. After the dynamite is wrapped up, packets of 2·5 kilos are placed in cardboard boxes, which are wrapped and tied round and filled in tens into wooden cases. For military purposes the cartridges are put directly into metal boxes with a socket in the lid for inserting the detonator. For use under water these metal boxes are sometimes used, and sometimes sausage-skins or rubber bags.

These cartridge buildings are usually small with light walls and roof ; only two or three operatives work in each, high earthen banks separating one man from the next so that the effects of an explosion may be mitigated.

In place of kieselguhr various other absorbents are used at the present time, *e.g.* wood meal (*cellulose*) mixed with inert mineral salts (calcium carbonate, sodium bicarbonate, &c.).

First in America and then in Austria *fulgurite* was prepared with 60 per cent. of nitroglycerine, the remaining 40 per cent. consisting of wheaten flour and magnesium carbonate. At Cologne, Muller prepared a *Wetter-dynamite* (*safety dynamite*, for use in mines containing firedamp ; *see later*) by mixing 10 parts of ordinary dynamite with 7 parts of crystalline sodium carbonate ; the water-vapour formed on explosion surrounds the flame and the explosive gases and thus prevents explosion of the firedamp. Many varieties of these dynamites are used to a greater or less extent in practice, *e.g. carbodynamite* containing 90 per cent. of nitroglycerine and 10 per cent. of carbonised cork, *sebastine, lithoclastite, carbonite*, &c.

Properties of Dynamite with Inert Bases. This forms a pasty mass of reddish yellow, red, or grey colour according to the quality of the infusorial earth employed ; to ensure a uniform colour about 0·25 per cent. of burnt ochre is often added. It is odourless and has the sp. gr. 1·4 and the pasty consistency of wet modelling clay ; the inside of the wrapper should show no traces of nitroglycerine (sweating). It is much less sensitive to pressure and percussion than nitroglycerine and, in small portions, can be lighted and burned without exploding.

It can, however, be exploded by powerful percussion or detonation, or by red-hot metal, or by heating suddenly to a high temperature or for a long time at 70° to 80°. Dynamite freezes at temperatures below + 8° and then becomes less sensitive ; before being used it must be carefully thawed in warming-pans, surrounded by water at a temperature not exceeding 60° ; it must never be thawed on a heated metal plate. Thawed dynamite should be used carefully as a little nitroglycerine exudes during thawing. Most of the dynamite made is used as an explosive in mines and for firearms ; for cannon it has little use, owing to the danger caused by sweating during the thawing, so that for military purposes explosives are used which are safer to transport and not so sensitive to shock or to discharge (explosion by sympathy).

II. **DYNAMITES WITH ACTIVE BASES.** (*a*) **Pulverulent Dynamites with Inorganic Nitrates.** Immediately after the discovery of dynamite with a silica base came the idea of replacing the inactive substance, which diminished the force of the nitroglycerine, by active substances so that the explosive power of the dynamite might be increased.

In America such dynamites are often made with 40 per cent. of nitroglycerine, 45 per cent. of sodium nitrate, 14 per cent. of wood-pulp, and 1 per cent. of magnesium carbonate ; these dynamites are well suited for mines where no great power but considerable safety is required. In Europe mixtures of nitroglycerine, ammonium nitrate, fine sawdust, sodium nitrate, carbon, &c., are made ; *e.g.* 20 per cent. nitroglycerine, 36 per cent. sodium nitrate, 25 per cent. ammonium nitrate, 18·5 per cent. roasted rye flour, and 0·05 per cent. soda.

In Austria Trauzl in 1867 prepared a pasty mixture of nitroglycerine with guncotton, which was not affected by water and was exploded only by fulminate of mercury detonators. This product was not successful, but similar and improved preparations were subsequently made.

About this time Abel in England prepared *glyoxiline* by soaking defibred guncotton and potassium nitrate in nitroglycerine ; this was also unsuccessful.

(*b*) **Blasting Gelatine and Gelatine Dynamite.** Since these contain nitrocellulose, they

will be mentioned later (*see* Smokeless Powders), after the manufacture of nitrocellulose has been described.

Statistics of dynamite : *see later* at the end of the chapter on Explosives.

NITROCELLULOSE

(Guncotton or Pyroxyline and Collodion-Cotton)

This substance should, to be in order, be described later, after cellulose (which is a carbohydrate with many alcoholic groups and with a molecular formula polymeric with $C_6H_{10}O_5$) has been studied, but as its properties and uses are closely connected with those of explosives, it is considered opportune to include it in the present section.[1]

CONSTITUTION OF NITROCELLULOSE. The relation $C_nH_{2m}O_m$ of the components of cellulose being expressed by the more simple formula $(C_6H_{10}O_5)_n$, it is found that the maximum degree of nitration consists in the introduction of three nitric acid residues per molecule of $C_6H_{10}O_5$, so that *guncotton* was given the name *trinitrocellulose*, and was represented by the formula $C_6H_7O_5(NO_2)_3$. Since the use of more dilute acids results in the combination of a less proportion of nitric acid residues, it is supposed that a *mononitro-* and a *dinitro-cellulose* are also formed.

It was found later by Eder that there exist nitrocelluloses with compositions intermediate to those of tri- and di-nitrocellulose, and others between the mono- and di-nitro-compounds, so that it must be supposed that cellulose has a formula at least double that of the simple one given above ; but the mononitrocellulose corresponding with this doubled formula, $C_{12}H_{20}O_{10}$, *i.e.* $(C_6H_{10}H_5)_2$, has not yet been prepared.

Still later Vieille, by accurate study of the nitrocelluloses prepared with acids of various concentrations, succeeded in preparing eight different types of nitrocellulose, this result indicating that Eder's formula, which predicted only six, could no longer serve. Vieille then proposed for cellulose a formula double that of Eder, *i.e.* $C_{21}H_{40}O_{20}$ or $(C_6H_{10}O_5)_4$, according to which twelve nitrocelluloses are theoretically possible ; eight of these, from endeca- to tetra-nitrocellulose have been actually prepared. Mendelejeff, having found nitrocelluloses intermediate to or identical with these twelve, but different from those studied by Vieille in being soluble in a mixture of alcohol and ether, proposed the doubling of Vieille's formula, so that cellulose becomes $C_{48}H_{80}O_{10}$ or $(C_6H_{10}O_5)_8$. To-day, however, it is thought that these differences are due to mechanical mixtures of the various nitro-

[1] In 1833 Braconnot observed that when starch or wood is treated with concentrated nitric acid, a mucilaginous solution is obtained which, on addition of water, yields a white powder soluble in a mixture of alcohol and ether ; this powder, which burns vigorously, he called *ayloidin* In 1838, by subjecting cotton to the same treatment, Pelouze obtained a product which exploded on percussion and was indeed nothing but *ayloidin* , he recommended it as highly suitable for the manufacture of fireworks. In 1845 Schonbein at Basle, and some months later, and independently, Bottger at Frankfort discovered that the nitration of cellulose takes place much more easily and completely if the cotton is treated with a mixture of concentrated nitric and sulphuric acids In order to utilise industrially the guncotton thus obtained, the two discoverers combined and kept their process secret After the initial difficulty in getting this new explosive taken up in practice, the extraordinary power of guncotton and its great advantages over black powder aroused considerable enthusiasm. But scarcely had it come into general use in various countries than a number of *spontaneous* and fatal explosions in *guncotton* factories and magazines, by which whole buildings were razed to the ground, created such a panic that its manufacture was everywhere abandoned. The process of nitration was then already known to Knop and Karmarsch, and to others, who manufactured guncotton by this simple process. And in 1846 Sobrero made use of the nitric-sulphuric mixture for the preparation of nitroglycerine

In 1853 the Austrian, Captain von Lenk, ascertained how to render guncotton safe. The Austrian Government acquired from Schonbein and Böttger the process of manufacture (at a price stated to be 30,000 florins, or £2500) and maintained the secret of avoiding the spontaneous decomposition of guncotton until 1862. Then von Lenk communicated the secret to the French and English Governments, and in 1864 patented the process in America. Whilst in America the manufacture was undertaken on an enormous scale, in Austria and England it was again suspended on account of further terrible explosions in the factories themselves ; these were explained by the English workers as due to the insufficient purification of the nitrocellulose by von Lenk. In 1865 Abel discovered the method of bestowing absolute safety and keeping qualities on the nitrocellulose He used first of all the process of washing proposed in 1862 by the Englishman J. Tonkin, which consisted simply in complete washing with abundant supplies of water ; the nitrated cotton was then defibred or *pulped* in machines similar to those employed in paper factories and the wet pulp subjected to considerable pressure. From that time the manufacture extended to all countries, in spite of an English factory being blown up in 1871 (apparently a criminal act), and in recent times it has acquired new and increased importance owing to the discovery of smokeless powder.

The process universally used at the present time in the manufacture of guncotton is that indicated by Abel. Before the discovery of smokeless powder, guncotton had limited applications and was not used in mines since, in the form in which it was prepared, it had an excessive shattering action, whilst in mines progressive explosives are usually required.

celluloses rather than to separate chemical combinations, and further, that the nitration is gradual and leads from the more simple to the more complex forms.

Nitrocelluloses with more than 12·83 per cent. of nitrogen were at one time regarded as being insoluble in alcohol-ether, but Abel showed that there are nitrocelluloses with 13·2 per cent. of nitrogen and still soluble in this mixture, whilst others with only 12·8 per cent. are insoluble ; and that this depends on the method of preparation—the duration of action of the mixed acids, the ratios and concentrations of the latter, and the temperature at which they act—and on the nature, purity, and dryness of the cotton. Only by following exactly the directions is it possible to obtain a constant percentage of nitrogen and complete solubility or insolubility in the mixture of alcohol and ether.

It was also once thought that guncotton was a *nitro-compound* in the true sense of the word, *i.e.* that the NO_2 groups were united directly to carbon. But first Béchamp and then others showed that it is a true nitric ester which can be saponified, with regeneration of the cellulose, by alkalis, alkaline salts, ammonium sulphide, or ferrous chloride. It has been further shown that with the maximum of nitrogen an oxynitrocellulose is obtained [oxycellulose is $(C_6H_{10}O_5)_3 + (C_6H_{10}O_6)_n$, so that the nitrocellulose will be $C_6H_7(NO_2)_3O_5 + C_6H_7(NO_2)_3O_6$, and this with ferrous chloride gives oxycellulose ; nitromannitol, treated similarly, gives mannitol and not oxymannitol].

PROPERTIES OF GUNCOTTON. Under the microscope nitrocellulose has the same appearance as ordinary cotton, but in polarised light it appears iridescent. When moistened with a solution of iodine in potassium iodide and then with sulphuric acid, nitrocellulose becomes yellow and cellulose blue. It is somewhat less white than ordinary cotton, is rather rough to the touch and crackles when pressed with the fingers ; it becomes electrified when rubbed and then appears phosphorescent in the dark. It is soluble in ethyl acetate, nitrobenzene, benzene, acetone, &c., but insoluble in water, alcohol, ether, acetic acid or nitroglycerine, although a mixture of nitroglycerine and nitrocellulose is soluble in acetone, forming a jelly, *cordite* (*see later*).

It resists the action of dilute acids, but is decomposed slowly by concentrated ~~sulphuric acid or~~ hot alkali, and completely by hot sodium sulphide. Decomposition is also effected by iron and acetic acid or by ammonium sulphide or ferrous chloride (Béchamp).

Flocculent, *loose* guncotton has the sp. gr. 0·1, whilst the powder (pulp) has the sp. gr. 0·3 and is exploded by shock or percussion only at the point where it is struck, the explosion not being propagated to the whole mass. When ignited, it burns so rapidly that even when it is placed on black powder, the latter does not burn.

In the form of cord, it burns more slowly and may be used as a rapid fuse. When wet or compressed it has a specific gravity varying from 1 to 1·3 (the absolute sp. gr. is 1·5) and it then burns slowly and cannot be exploded by percussion or by ordinary detonators ; explosion can, however, be induced by detonating a little dry guncotton with a fulminate of mercury cap. The decomposition proceeds according to the equation :

$$2C_6H_7O_2(ONO_2)_3 = 5CO + 7CO_2 + 8H + 3H_2O + 6N.$$

Less compressed guncotton gives more CO and H in comparison with the CO_2 and H_2O, and hence has a less effect, the development of heat being smaller. No ash or smoke is formed, and 1 kilo of guncotton yields 741 litres of gas (the water being liquid, or 982 litres if the water is in the state of vapour), which is inflammable and, owing to the presence of carbon monoxide, poisonous. The temperature of combustion has been given as 6000° (*i.e.* 1071 Cals. are developed by 1 kilo).

Unless guncotton is carefully prepared, it undergoes gradual change and may explode spontaneously, especially in the light, and to this are probably

due the great explosions which occurred formerly (1848–1862) Even dry, granulated guncotton becomes harmless and safe to handle if it is immersed for a moment in ethyl acetate, as it becomes coated with a gelatinous layer which dries it and preserves it, if moist, from further evaporation.

Guncotton is transported in large quantities in the wet state in wooden boxes placed in others of zinc which are sealed hermetically to retain the moisture. It is stored in dry magazines which are situate at least 150 metres from any habitation and are not surrounded by earthworks so that the more serious effects due to projection of *débris* may not be added to those of an explosion.

MANUFACTURE OF GUNCOTTON. Hanks of purified cotton, free from impurities, are employed. This cotton should fulfil certain requirements.[1]

The *pure* cotton is placed loose on trays which are arranged in a drying-stove heated by means of gilled pipes through which steam circulates; the heating is continued until the proportion of moisture is less than 0·5 per cent., after which the cotton is allowed to cool for 12 to 15 hours in hermetically sealed boxes. If not pure the cotton is best defatted by boiling it for 2 to 3 minutes with 2 per cent. sodium hydroxide solution; it is then washed with water and subsequently treated with very dilute nitric acid in the hot. In some cases it is also bleached with a weak solution of hypochlorite, well rinsed with water and dried in a hot-air oven as above. When almost dry it is carded, dried completely, and, while still hot, placed in hermetically sealed boxes so that no more moisture may be absorbed.

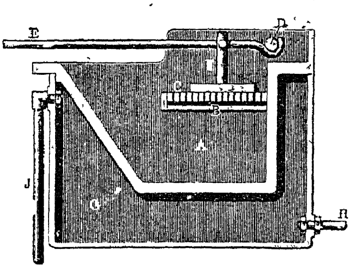


FIG. 188.

Nitration is then effected with a mixture of concentrated nitric and sulphuric acid, as follows: 3 parts of pure sulphuric acid of sp. gr. 1·841 (96 per cent.) are poured into 1 part of pure nitric acid of sp gr. 1·516, mixing taking place immediately and completely without the aid of stirrers. The mixture is then delivered with the help of an acid elevator (*Montejus*) into the nitration apparatus, consisting of a cast-iron vessel, *A* (*dipping pot*) (Fig. 188), standing in a larger vessel, *G*, through which cold water circulates from *H* to *J*. The cotton is immersed in small portions (300 to 800 grms.) in the acid-bath and is stirred with an iron fork. In England 1 kilo of cotton is used per 160 kilos of the acid mixture, while in Germany 1 kilo of cotton is taken for every 40 kilos of acid; after a short time (15 to 30 minutes) the nitrated cotton is removed with iron forks and is placed to drain on a cast-iron grid (grate), *B* and *C*, arranged on one side above the vessel; before it is taken away, it is pressed with a cast-iron plate, *F*, connected with a lever, *D E*.

The acid mixture is renewed when it has treated 30 to 50 per cent. of its weight of cotton; also after each portion of cotton is removed from the bath, fresh acid mixture, equal to ten times the weight of the cotton taken out, is added in order to make up for what has been absorbed and combined. On the German system (where less acid is used) renewal takes place more frequently. Above each of the nitrating vessels is a hood with a strong draught to carry off the nitrous vapours which are always evolved. Excessive rise of temperature gives a guncotton which contains less nitrogen and shows less complete insolubility in alcohol-ether than are required in practice.

In some factories the nitration is carried out in a number of small, deep and narrow, hemispherical vessels of cast-iron mounted on trolleys. These are charged in order with certain weights of acid mixture (30 to 50 kilos) and dry cotton (2 to 4 kilos), and, after thorough mixing, the trolleys are pushed into an oblong lead-lined chamber provided with

[1] *Cotton* for nitrocellulose should be pure white and should not contain dust or fibres of jute, hemp, or flax, or woody matter or pods; these impurities, when separated by hand from 200 grms. of the cotton, should not exceed 0 5 grm. The filaments should not be too short, otherwise they form a paste during nitration. A small piece thrown into water should sink in two minutes. It should not contain more than 0 9 per cent. of substances soluble in ether (fats, &c.); in many factories 0 5 per cent. is not allowed. In England the amount of fat allowed is 1 1 per cent extracted with ether in 4 hours in a Soxhlet apparatus (*see* Analysis of Fats). The moisture, determined by heating the cotton in an oven at 100° until its weight remains constant, should not exceed 6 per cent. and the cotton merchant is debited with any excess and also with the cost of drying.

When moistened with a few drops of water, the cotton should maintain a neutral reaction.

The ash, estimated by heating a few grammes of the cotton to redness in a platinum capsule until it becomes quite white and of constant weight, should not amount to more than 0·3 per cent.

as many doors as there are trolleys. A powerful aspirator draws the nitrous vapours into a wooden flue. A battery of soaking-pots is used in such a way that when the last is introduced into the chamber the first has already finished reacting (30 to 40 minutes), and as the pots are of metal and relatively small and are in a strong draught, the heat developed is readily dispersed. The pots are removed from the chamber and taken to the neighbouring centrifugal machines, into which the contents of the pots, which are mounted on pivots, are tipped. The centrifuges are similar to those employed in sugar factories (*see* Sugar) and have a steel or leaded steel rotating basket; aluminium ones have also been tried but not with great success. A few minutes' centrifugation at 1000 revolutions per minute removes the greater part of the acid from the guncotton; the latter is immediately taken to the washing machines, while the acid recovered is revivified in the manner described on p. 227. If drops of water or lubricating oil fall on to the cotton during centrifugation, the mass sometimes undergoes sudden decomposition with formation of a dense cloud of brown vapour; this does not constitute a serious danger, since usually it is not accompanied by explosion.

In some factories the nitration is nowadays carried out directly in the centrifuges, which may be of naked or leaded steel or even of earthenware, although these are heavier

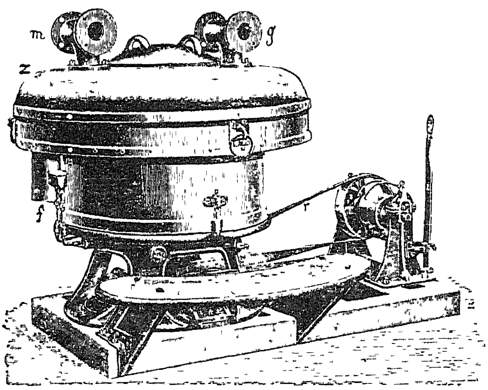


FIG. 189.

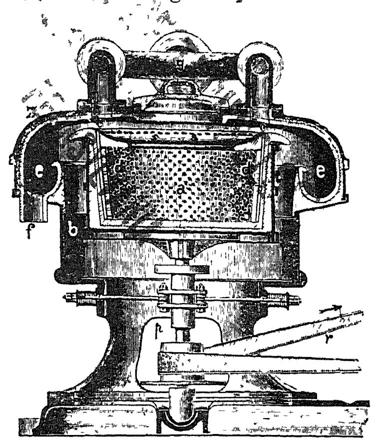


FIG. 190.

and more fragile (*see* Figs. 189, 190). The latter consist of a double-walled earthenware basket, the inner wall, *d* and *a*, but not the outer one, being perforated; the two walls being a slight distance apart, an annular space, *c*, is left, which has an outlet above in a number of holes, *s*, in the edge of the bush. The whole is bound with steel hoops, *t*, to prevent danger from projection in case of fracture. The dry cotton (7 to 8 kilos or more) is arranged peripherally inside the perforated basket, the acid being supplied by the tube, *m*; the basket, surrounded by the jacket, *b*, and the cover, *z*, both of earthenware, is set in motion by the shaft, *p*, driven by the belt, *r*. The acid is driven uniformly through the cotton by centrifugal force, rises through the ring space, *c*, and issues from the holes, *s*, into the channel, *e*, whence a pipe, *f*, carries it to an elevator to be again circulated. The operation is of short duration, and the red vapours are emitted from the tube, *g*. During nitration, the velocity of the drum is relatively low, but at the end the velocity is increased; the nitrated cotton can then be taken away at once to be washed.

Use is, however, preferably made of steel centrifuges with circulation of the acid, as proposed by Selwig and Lange; the basket, *d*, is perforated (Fig. 191) and the cover is of aluminium and hinged and is furnished with a large tube, *o*, communicating with the pipe of an aspirator, *n*. The basket is moved slowly and filled with the nitric-sulphuric mixture (*e.g.* 70 per cent. H_2SO_4, 23 per cent. HNO_3 and 7 per cent. water) up to the top edge; the cotton is then introduced in packets (1 kilo per 50 kilos of acid) and the basket given a velocity of 20 to 30 turns per minute. This movement causes the acid to circulate continuously through the cotton, and in half an hour the nitration of 6 to 8 kilos of cotton is complete; the acid is then discharged and the velocity increased to remove as much acid as possible from the cotton, which is taken out and washed in the ordinary way.

Excessive prolongation of the centrifugation and excessive velocity are not only without advantage but involve increased danger of explosion.

From August 1905 in the Royal Gunpowder Factory at Waltham Abbey (where 2000 tons are produced per annum), guncotton has been made by the *displacement process* of J. M. and W. Thomson and Nathan, which is briefly as follows.

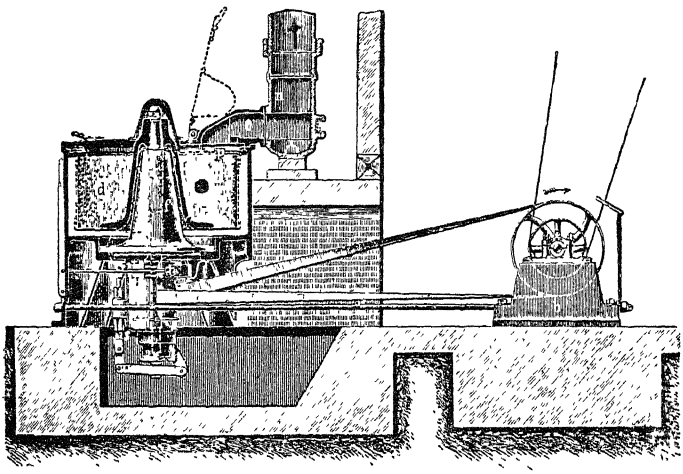


FIG 191.

Into the earthenware basins, which are furnished with aluminium covers (Fig. 192) and are connected in groups of four by means of leaden pipes and also communicate with exhausters, 600 litres of the nitric-sulphuric mixture are placed; about 10 kilos of cotton are then introduced in small portions into each vessel and are pressed with perforated wrought-iron plates. The nitration lasts two and a half hours, and at the end water is introduced above the perforated plate, this displacing at the bottom a corresponding quantity of the acid; the acid thus recovered is reinforced with oleum and strong nitric acid. The displacement lasts 3 hours, after which the mass is centrifuged and the cotton washed, rendered stable, pulped, &c.

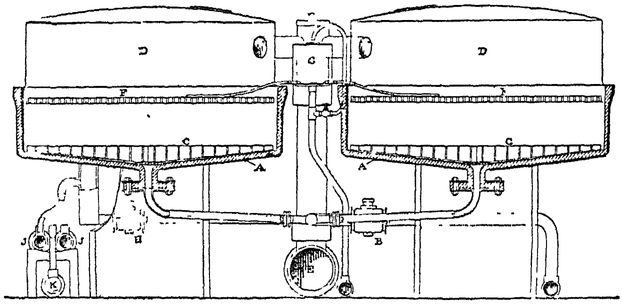


FIG. 192.

Since guncotton should have a very definite nitrogen content, different from that of collodion-cotton used to gelatinise nitroglycerine (*see later*), the process of nitration is carefully followed by numerous rapid analyses until suitable conditions are found for obtaining a constant product; after this has been done, the final control is sufficient. It has been proposed to follow the extent of nitration of cellulose by observing its behaviour towards polarised light. In recent years it has been shown that guncotton of more constant type and more readily rendered stable is obtained if the acid mixture is renewed for each nitration; the last processes described are hence to be preferred.

WASHING. The nitrocellulose from the centrifuge is passed directly into the oval washing vessel (*see* Fig. 193), which has a longitudinal partition down the middle (like the hollander machines used in paper-making), and in which a shaft furnished with beaters

mixes the whole mass with water; the latter is constantly renewed and the washing continued until the acid reaction towards litmus paper disappears (2 to 3 hours). The washed guncotton is either centrifuged again or put to drain in wooden baskets. Although it no longer exhibits an acid reaction, yet, as was shown by J. Tonkin in 1862 and by Abel in 1865 (in England), it still contains acid or rather unstable sulphuric esters in the small channels of the fibres.

To separate these remaining traces of acid, the nitrocellulose is rendered stable by boiling it for two consecutive periods of 12 hours each with water in wooden vats fitted with perforated false bottoms (one vat holds even more than 1000 kilos of the cotton), beneath which steam is passed. Then follow four more boilings of 4 hours each with water (formerly one or two boilings with calcium carbonate were also carried out), and finally two or three boilings each of 2 hours with fresh water. This system of washing was proposed by Dr. Robertson and employed with advantage in the Government Factory at Waltham Abbey; it lasts altogether 48 hours, is preferable to that in which the boilings are short at the beginning and long at the end, and especially to that where boiling with soda is interposed, as the soda hydrolyses the nitrocellulose and transforms it partially into collodion-cotton poor in nitrogen and soluble in alcohol-ether.

Some of the boiling may be dispensed with if the nitrocellulose is steamed in closed vats.

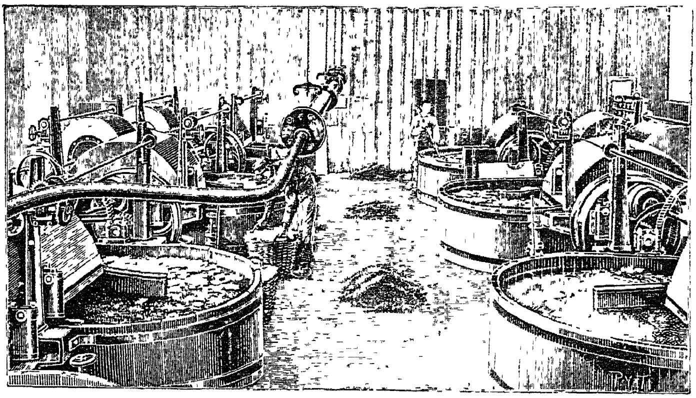


FIG. 193.

PULPING. In spite of all the washing and boiling to which it is subjected, the guncotton persistently retains a trace of acid, and to remove this, the cotton is thoroughly defibred (*pulped*) as was proposed by Tonkin and by Abel in 1865. This operation is carried out in hollanders similar to those used for the preceding washing and identical with those used in the manufacture of cellulose for paper (*see later*, section on Paper, for figures and cross-sections).

Pulping lasts from 5 to 8 hours, according to the fineness required, but if it is incomplete, inconveniences are met with in the subsequent compression, the desired density not being attainable; also if pulping is carried too far, the compression is disturbed in another way. Guttmann proposed the use of hot water in pulping, and this possesses several advantages in addition to saving time. In the large wooden vats, as much as 200 kilos of guncotton can be treated at one time. In some cases a little calcium carbonate is added to guncotton to preserve it and to neutralise any residual acid; it is added in powder just before the completion of pulping.

If the guncotton thus prepared does not answer the rigorous tests to which it is subjected (*see later*, Tests of Stability), it is rendered stable by again boiling it for some hours with water in large wooden tanks (sometimes lined with lead), jets of steam, and also of air to keep the mass moving, being passed in. In order to separate the water, the mass is placed in suitable centrifuges fitted with drums of fine metal gauze entirely surrounded by linen; in other cases, the water is separated as in paper-mills by placing the mass in chambers having perforated brass floors covered with cloth, the pulp drained in this way being finally centrifuged. The water separated from the pulp is allowed to stand in suitable vessels to deposit the finer fibres it has carried away. After centrifugation, the pulp contains about 25 to 30 per cent. of water and in this state it can be kept safely in zinc boxes, in

which it can be transported if it is slightly compressed and the cover of the box soldered. If properly prepared, guncotton should not contain more than 3·5 to 4 per cent. of collodion-cotton (soluble in alcohol-ether), but in England 7 to 8 per cent. is allowed.

COMPRESSION OF GUNCOTTON. For military purposes, that is, for cartridges and for the blocks used for charging torpedoes, the still moist guncotton is strongly compressed to render it safer and more powerful owing to the increased charging density (*see above*), which reaches the value 1·2 with pressures of 500 to 1000 atmos. Fig. 194 shows in section a Taylor and Challen hydraulic press used for this purpose ; this is set up in an isolated room and can be controlled from a distance so as to avoid any great amount of damage in case of explosion during the compression, this mostly happening if any hard foreign body chances to be present in the guncotton.

To obtain the greatest density, the pulp is first washed with hot water and slightly compressed in the mould, *d*, by means of the lever, *h*, the water being drawn away under the perforated base, *c* (covered with steel gauze), by a pump connected with the tube, *b*.

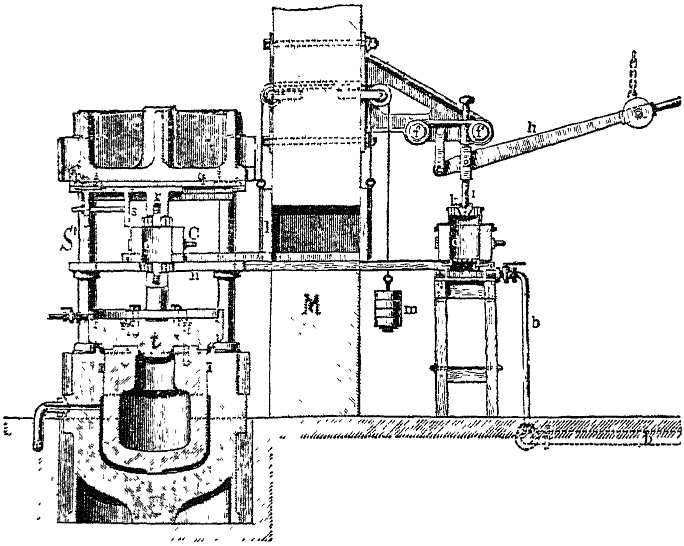


FIG. 194.

The partitions, *l*, are raised and the mould passed through an aperture in the wall, *M* (which serves as a protection for the workmen), and thus above the plate, *n*, of the hydraulic press ; this plate is kept horizontal by four columns, *S'*. The mould is raised by the piston, *t*, of the press so that it is pressed against a die, *r*, fixed to the cover, *q*. This cover is held fast by the four columns so that the die penetrates the mould and compresses the cotton under a pressure of 800 to 1000 atmos. The degree of humidity after the compression is about 10 per cent., and at each operation a block of 1 kilo is made, the shape being adapted to that of the projectile. Thus compressed, guncotton is so hard and compact that it can be worked quite safely with the plane, saw, or boring tool, a fine jet of water being directed at the point where the cutting is taking place. To prevent compressed guncotton from losing moisture and from becoming mouldy, it is dipped in molten paraffin wax ; or, better, it is immersed for a moment in ethyl acetate (or acetone), which dissolves a little nitro cellulose at the surface and forms a kind of impermeable varnish.

The theoretical *yield* of dry guncotton is 185 kilos per 100 kilos of dry cotton ; practically 171 to 176 kilos are obtained.

USES OF GUNCOTTON. For the charging of torpedoes, moist compressed guncotton has replaced all other explosives. It is used also for filling grenades, which are then covered with molten paraffin wax to unite the grenade and the explosive ; explosion is effected by a detonator of dry guncotton. It is made also into compressed cartridges for use in mines, a cavity being left for the detonating cap and the fuse.

Mixtures of granulated guncotton and nitrates are placed on the market under the names of *tonite*, *potentite*, &c. Abel obtained beautiful pyrotechnic effects by saturating guncotton with solutions of various mineral salts capable of imparting different colours to the flame. It is sometimes used for filtering acids, alkalis, and solutions of permanganate, being resistant to these reagents in the cold. Also it is in some cases employed as an electric insulator and for bandaging purulent sores and wounds, being first saturated with potassium permanganate.

COLLODION-COTTON FOR GELATINE DYNAMITE, DYNAMITE, AND SMOKELESS POWDERS. During recent years, a different, less nitrated nitrocellulose, *collodion-cotton*, has assumed very great importance in the manufacture of smokeless explosives. On the other hand, guncotton itself has, of late years, been largely replaced by compressed, crystalline, or fused *trinitrotoluene* (*see* Part III), especially for military and naval purposes. Collodion-cotton was at one time thought to be dinitrocellulose, soluble in a mixture of alcohol and ether, but it has now been shown to be a mixture of various soluble nitro-compounds, which are formed under different conditions from those yielding guncotton. Collodion-cotton should have a constant nitrogen-content, and it should be readily soluble in a mixture of alcohol (1 part) and ether (2 parts), giving a dense viscous solution. If it answers these requirements, it gelatinises nitroglycerine well and dissolves completely in it; attention is, however, also paid to the time necessary for gelatinisation.

For photographic plates, extensive use was formerly made of ethereal-alcoholic solutions of soluble nitrocellulose (collodion), and in this case importance was attached not so much to the viscosity as to the proportion of nitrocellulose which would yield an elastic film of marked resistant properties. For this purpose, the nitration is carried out at a temperature of at least 40° to 50°, so that the resulting collodion is less viscous; also the nitrocellulose is not pulped.

The cotton is immersed for 60 to 90 minutes in a mixture of 1 part of 96 per cent. sulphuric acid (sp. gr. 1·840) and 1 part of 75 per cent. nitric acid (sp. gr. 1·442) at a temperature of about 40°.

The more concentrated the acid and the more prolonged its action, the higher will be the nitrogen-content, but the viscosity will not be decreased; a high temperature, however, results in diminution of the proportion of nitrogen and also of the viscosity.

The nitration can be effected in the cold, but more concentrated acids and more prolonged action are then required. After nitration collodion-cotton intended for the manufacture of gelatine dynamite goes through all the operations of washing, pulping, and boiling employed with guncotton.

Collodion cotton for gelatine dynamite or smokeless powder must be subjected to a *drying* process. Since the centrifuged pulp still contains 30 per cent. of water, whilst nitrocellulose begins to decompose at 70° (or even at 50° if badly prepared) and in the dry state is very sensitive to shock or percussion, the drying of collodion-cotton constitutes a very dangerous operation. At one time it was dried by means of indirect steam, but nowadays it is placed on iron plates heated to 40° to 50°. When dry, it sometimes becomes electrified on rubbing, and this phenomenon explains the frequent spontaneous fires formerly occurring in the drying ovens. Guttmann prefers to dry the collodion-cotton on copper plates connected with the earth by wires (to discharge the electricity). These plates are perforated with conical holes 0·25 mm. wide at the top and 1 mm. at the bottom; strips of leather are used to prevent rubbing of the metal parts. In these ovens, the pulp is spread out and is subjected to the action of a current of air heated to 40° (in some cases, also dried) and in two days the mass is dry, not more than 0·1 per cent. of moisture being then present. The dried material is then carefully placed in rubber bags and stored in air-tight boxes.

The drying ovens are provided with alarm-thermometers, which also regulate the temperature automatically.

Drying in a vacuum is also employed (especially with fulminate of mercury) and is then more rapid and takes place at a lower temperature, while the danger of an explosion is diminished owing to the absence of the tamping effect of the atmospheric pressure (*see* p. 221).

Collodion-cotton for making ballistite (*see later*) should contain 11·75 to 11·95 per cent. of nitrogen, whilst that for ordinary gelatine dynamites contains as much as 12 per cent.

SMOKELESS POWDERS. Even 50 years ago attempts were made to diminish the smoke produced by ordinary gunpowder by diminishing the amount of sulphur present, but its relations to the nitre and carbon cannot be greatly altered. Potassium nitrate was then replaced by ammonium nitrate, but this was found to be too hygroscopic ; yet later, ammonium picrate was employed with better, but still not satisfactory, results. In 1864 Schulze prepared a smokeless powder from nitrocellulose obtained from pure wood-cellulose. It gave good results with sporting guns, but was too shattering for use in warfare, and the same was the case with a smokeless powder prepared in 1882 by Walter Reid by granulating nitrocellulose and gelatinising it superficially with alcohol and ether.

The true solution of this important problem is due to Vieille, who in 1884 found that the *shattering* action of guncotton could be transformed into a *progressive* (or *propellant*) action by destroying the fibrous structure with suitable solutions. To attenuate the rapidity of explosion of guncotton it must be made as dense as possible (theoretically the fibre free from interstices has the density 1·5) and this cannot be done practically with fibrous cotton (even when pulped) as a pressure of 4000 atmospheres would be necessary. Vieille, however, dissolved or gelatinised the nitrocellulose and then recovered it by evaporating the solvent.

With the smokeless powder prepared by Vieille in 1885 the velocity of projectiles from cannon was increased by 100 metres per second over that obtained with ordinary powder, the pressure in the cannon being the same in the two cases ; hence guns of smaller calibre could advantageously be employed.

This amounted to a revolution in the region of ballistics, since, in addition to the advantages of no smoke or ash, and of the use of lower calibres, there was also the possibility of charging empty projectiles with these explosives, which are made and kept so safely. Gelatinisation is effected by solvents of nitrocellulose, *i.e.* by ether, acetone, ethyl acetate, nitroacetylglycerine, &c. (*see* p. 223).

I. SMOKELESS POWDERS OF PURE NITROCELLULOSE. The quantity of dry nitrocellulose (6 to 10 per cent. of the weight of solvent) decided on is introduced into the kneading machine (*see* p. 243), which is furnished with a cover, the necessary quantity of solvent being then added and the kneading continued for 6 to 8 hours ; no danger of explosion attends this process. If a mixture of alcohol and ether is employed as solvent, less highly nitrated cellulose (collodion-cotton) may be used ; the 30 per cent. of water in the moist, centrifugated collodion-cotton is first displaced by alcohol and the mass then centrifugated again, the amount of alcohol remaining in the cotton being calculated so that the quantities of ether and alcohol required in the kneading machine may be known. This procedure offers the great advantage of avoiding the very dangerous drying of the collodion-cotton. When the gelatine in the kneading machine is homogeneous and cold, it is taken to the rolls, which are similar to those employed for ballistite (*see later*).

The principal object of *rolling* is to increase the density of the gelatine and to give it a uniform composition. It is carried out between ordinary cylindrical rolls with increasing pressure, so that with repeated rollings between different rolls, sheets varying in thickness from half a centimetre to a fraction of a millimetre can be obtained. The rolls are heated by means of steam to a temperature not exceeding 60°, so that the solvent is gradually eliminated from the whole mass. One of the most commonly used rolling machines for thick sheets is shown in Fig. 195 and one for thin sheets in Fig. 196. In France preference is given to hydraulic presses which give a still more uniform product.

The thin sheets can then be cut into fine strips by means of rollers with superposed knives, as shown in Figs. 197 and 198. Some machines give a product like cut tobacco. If the strips, as they issue from the machine, are passed under other cutters perpendicular to the first, pieces of various lengths or cubes can be obtained which are convenient to carry and to use.

Since these smokeless powders still contain small quantities of free solvent the cut pieces are dried in a well-ventilated oven at about 40°. This drying is now carried out more rapidly and with less danger in a vacuum (*see* p. 239).

II. SMOKELESS POWDERS OF NITROCELLULOSE AND NITROGLYCERINE.

A. As we have already seen, in dealing with the theory of explosives, the explosion of nitroglycerine is accompanied by the liberation of unused oxygen ; on the other hand, it

is known that guncotton does not contain sufficient oxygen for the complete combustion of the carbon and hydrogen present in the nitrocellulose molecule.

In 1875, A. Nobel conceived the happy idea of associating the two substances by dissolving in nitroglycerine a certain quantity of soluble nitrocellulose, that is, that used in the manufacture of collodion. This procedure gives gelatines of varying consistency

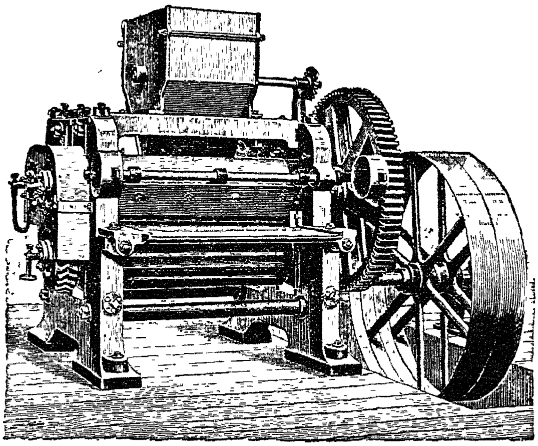


FIG. 195.

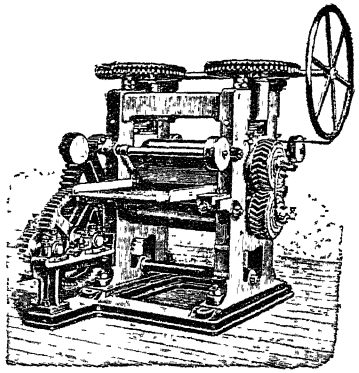


FIG. 196.

according to the quantity of nitrocellulose (collodion-cotton) dissolved. *Blasting gelatine* is made from 90 to 93 per cent. of nitroglycerine and 7 to 10 per cent. of dry collodion-cotton ; *gum dynamites*, on the other hand, contain about 97 per cent. of nitroglycerine and 3 per cent. of collodion-cotton, and when they are mixed with about one-third of their weight of absorbent substances (wood-meal, rye-flour, sodium or ammonium nitrate) they

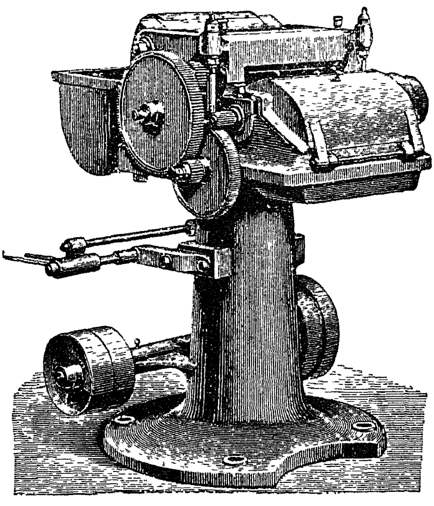


FIG. 197.

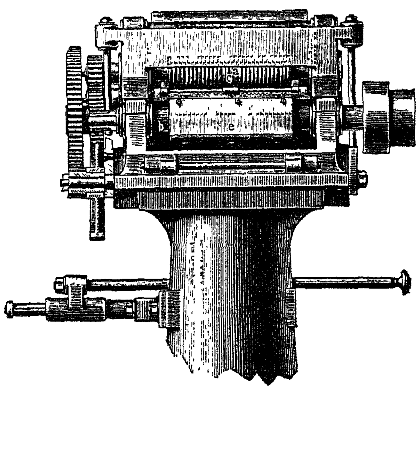


FIG. 198.

form the *gelatine dynamites*, which are still plastic, although less so than the gum dynamites, and are also less violent and hence serve well for mining purposes. A common type of gelatine contains, for instance, 62·5 per cent. of nitroglycerine, 2·5 per cent. of collodion-cotton, 25·5 per cent. of sodium nitrate, 8·75 per cent. of wood meal, and 0·75 per cent. of sodium carbonate ; it has a specific gravity of 1·5, is exploded with a No. 1 fulminate of mercury cap, and is sold in Austria for No. I dynamite, whilst *gelignite* is sold for No. II dynamite and contains 45 to 50 per cent. of gum dynamite and about 50 per cent. of absorbents as above.

At Christiania a non-congealing *gum dynamite* is made from blasting gelatine and a little nitrobenzene and ammonium nitrate; it has a specific gravity of 1·49 and is less effective than the gelatine dynamites.

For military purposes (torpedoes, cannon, &c.), as much as 4 per cent. of camphor is added in Italy, Austria, and Switzerland; these gelatines are thus rendered insensitive and very safe, and they require special detonators (*e g.* a mixture of 60 per cent. of nitroglycerine and 40 per cent. of collodion-cotton or compressed guncotton).

In certain commercial products the collodion-cotton is replaced by nitrated wood or straw, while nitrobenzenes, nitrotoluenes (especially liquid dinitrotoluene), &c., are used instead of nitroglycerine.[1]

Gelatine and gum dynamites have the appearance of plastic masses, the latter, which has the sp. gr. 1·6, being especially horny and translucent. Gum dynamite sometimes exudes a little nitroglycerine and so loses in shattering force; when heated for a long time at 70°, it swells up, becomes spongy and decomposes with formation of red, nitrous vapours; it sometimes ignites in metal boxes when exposed to the sun. It is less sensitive even than dynamite (about six times less) to percussion and special caps of gelatine dynamite are required to explode it. It serves well for use in war, since it is insensitive to discharges, and to render it still less prone to detonation by influence it is mixed with a little camphor. When 20 per cent. of collodion-cotton is dissolved in nitroglycerine, a gum dynamite is obtained which is not exploded by the most powerful caps. And ballistite, which contains 30 to 50 per cent. of collodion-cotton, requires special detonators. After freezing and thawing, it becomes more sensitive and dangerous, as is the case with dynamite. It has a greater shattering power than dynamite and acts better than this under water, which does not wash away the nitroglycerine so easily. Exudation of nitroglycerine occurs more readily than with dynamite and causes some degree of danger. It is used as a basis for the manufacture of smokeless powder. Gelatine dynamite is safer to handle and store than ordinary dynamite, which it is largely replacing.

The *manufacture* of these *gelatinised dynamites* requires collodion-cotton, which is very carefully prepared and is completely soluble in a mixture of alcohol and ether, in addition to which it must possess as great a proportion of nitrogen as possible. When it

[1] It is impossible at the present time to compare the various commercial brands of dynamite of different countries or even of one country, so varied are the types and the ratios of the components, sometimes when the commercial name is the same Thus No 1 *ammonia dynamite* (French) contains 40 per cent of nitroglycerine, 45 per cent. of ammonium nitrate (this, when pure, is not hygroscopic), 5 per cent of sodium nitrate, and 10 per cent. of wood-meal or wheat-flour, the No 2 quality of the same brand contains 20 per cent of nitroglycerine, 75 per cent. of ammonium nitrate, and 5 per cent of wood-meal In *Germany*, the name **Gelatine Dynamites** is given to all mixtures prepared from *explosive gum* (96 per cent nitroglycerine gelatinised with 4 per cent. collodion-cotton and a nitre-base as absorbent. In *England*, however, No 2 *gelatine dynamites* are called *gelignites*, and are often formed of 65 per cent of the gum and 35 per cent of absorbents (75 per cent nitre, 24 per cent. *wood-meal*—wood-pulp used for paper, in a dried state—and 1 per cent of soda) In *Austria*, *dynamite I* is made from 65 5 per cent. of nitroglycerine, 2·1 per cent of collodion-cotton, 7·41 per cent of wood-meal, 24 85 per cent. of nitre, and 0 26 per cent. of soda; *dynamite II* contains 46 per cent of nitroglycerine, &c, and *dynamite II A*, 38 per cent. of nitroglycerine, &c. In France, gelatine dynamites are called *gums*, and are prepared in very varied forms, *e.g. gum MB* with 74 per cent. of nitroglycerine, *gum D* with 69 5 per cent, and *gum E* with 49 per cent; then there are *dynamite gelatiné* 1, 2*a*, 2*b*, and 2*c* (the last with 43 per cent. of nitroglycerine, &c), &c In *Belgium*, gelatine dynamites are called *forcites*, *forcite extra* contains 74 per cent. of nitroglycerine, *superforcite* 64 per cent., *forcite* No 2, 36 per cent., &c

In *England* the types most commonly used are: *dynamite No. I*, with 75 per cent of nitroglycerine; *gelignite* with 65 per cent of gelatinised nitroglycerine (97 per cent of nitroglycerine), 25 per cent. potassium nitrate and 10 per cent wood-meal; *blasting gelatine* with 93 per cent of nitroglycerine and 7 per cent. of collodion-cotton; *gelatine dynamite* with 80 per cent. of gelatinised nitroglycerine (with 3 per cent. of collodion-cotton), 15 per cent. of potassium nitrate and 5 per cent of wood-meal.

In *Italy* there is *dinamite-gomma A* (or simply *gomma A*, corresponding with the French *gomme extra-forte*) formed from 92 per cent. of nitroglycerine and 8 per cent. of collodion-cotton; *gomma B* (corresponding with the French *gomme a la soude*) with 83 per cent. of nitroglycerine, 5 per cent. of collodion-cotton, 8 per cent. of sodium nitrate, 3·7 per cent of wood-meal, and 0 3 per cent of sodium or calcium carbonate or ochre. Commercially, however, the strength is given in terms not of nitroglycerine but of *gelatine*, that is, the starting material is taken as a gelatine formed by gelatinising 94 per cent of nitroglycerine with 6 per cent of collodion-cotton, to which are then added the various absorbents; thus gomma *B* contains 88 per cent. of gelatine (equivalent to 83 per cent. of nitroglycerine). In Italy the old kieselguhr dynamite is no longer used and is replaced by the so-called *gelatine-dinamiti*, which are marked with various letters and numbers, thus *No* 0, containing 74 per cent. nitroglycerine, 5 per cent collodion-cotton, 15·5 per cent. sodium nitrate, 5 per cent. wood-meal, and 0 5 per cent. carbonates; *G. D. No.* 1, with 70 to 72 per cent. nitroglycerine, &c.; *G. D. No* 2, with about 48 per cent. nitroglycerine, and *dinamit No.* 3, with 25 per cent. nitroglycerine, 54 per cent. sodium nitrate, 19 per cent. wood-meal and cellulose, and 2 per cent. soda and yellow ochre. During recent years there have also been prepared in Italy *gelatine-dinamiti*—suggested by Dr. Leroux—with 8 to 10 per cent. of the nitroglycerine (of No. 1) replaced by as much *liquid dinitrotoluene*, which gelatinises cotton well and gives non-congealing dynamites, more economical and almost as powerful as, sometimes more powerful than, the corresponding gelatine dynamites; these act well in open mines, but give large quantities of unpleasant fumes, and hence are unsuitable for use in galleries, &c.

is not well prepared, although it dissolves in alcohol and ether, it is not readily and entirely soluble in nitroglycerine, or it does not retain the latter completely for a long time. The quality of the collodion-cotton depends, then, on the choice of a good cotton and on exact conditions of nitration—duration, purity of acids, temperature.

This should then be finely subdivided (*pulped*) and dry, so that it can be passed through a fine sieve before being mixed with the nitroglycerine, in which it does not dissolve well if moist. This operation of gelatinisation and kneading is termed in French *pétrinage.* The necessary quantity of nitroglycerine is placed in wide, shallow vessels of copper or lead heated externally by hot water (50° to 60°). After 30 to 60 minutes, when the temperature has reached 45° to 50°, the required amount of dry, powdered collodion-cotton is added in small quantities and mixed now and then with a wooden spade. It is then left for a couple of hours and afterwards thoroughly mixed by hand, just as dough is mixed, so as to form a homogeneous, soft paste; this, on cooling, forms a more or less hard, elastic, translucent gelatine which constitutes the gelatine or explosive gum. If, instead of collodion-cotton alone, absorbents are also used, *gelatine dynamites* are obtained; these are converted into rolls and cartridges with the machines already described (p. 230). When the gelatine is not intended for the manufacture of ballistite (*see later*), the conversion into cartridges is effected by means of an Archimedean screw machine (*boudineuse*), similar to sausage-making machines (Fig. 199).

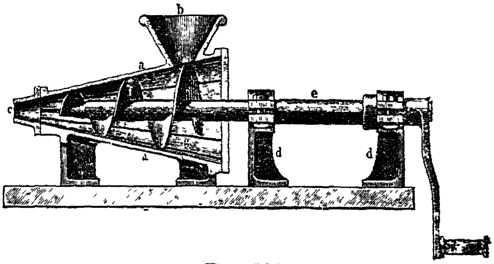


FIG. 199.

The *mixing* for causing gelatinisation, especially if other substances besides collodion-cotton are added, can be carried out in mechanical kneading machines (Fig. 200) mounted on a wooden platform, *b*, which can be raised by screws and cog-wheels, *g*, *e*, and *h*, resting on supports, *a a*; on this platform is a double-walled, copper pan, *i j*, which can be surrounded with hot water and can be moved on rollers. Above are the bevel-wheels and pulleys for working the stirrers, *q* and *r*. The nitroglycerine is first heated to 50° by raising the temperature of the water in the jacket of the copper pan, the latter being then raised so as to submerge the stirrers; the ingredients necessary to give the required type of gelatine dynamite are then added. Mixing is complete in an hour. Other forms of kneading machine are used, *e.g.* the Werner-Pfleiderer machine, which is employed for smokeless powders and for bread-making. After cooling, the plastic dynamite, which has a yellowish, translucent appearance, is removed from the kneading machine to a separate building to be converted into cartridges. This is done in special machines (*boudineuses*) (Figs. 201 and 202), furnished with endless screws, which force the dynamite or gum from a hole, *B*, in continuous rolls, these being collected in definite lengths in a casing of parchment paper or paraffined paper, *C*.

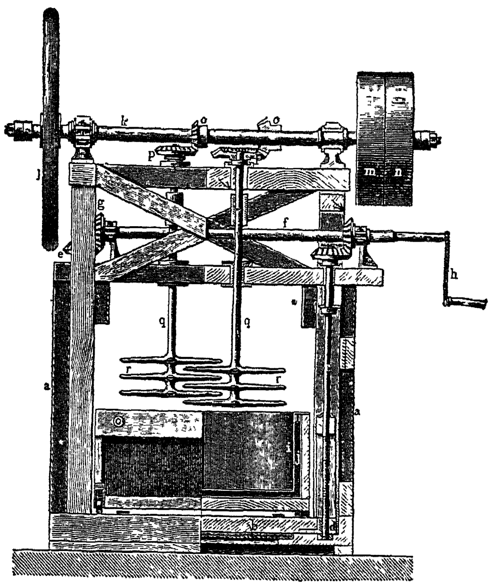


FIG. 200.

B. Military Smokeless Powders. These approach the gum dynamites in character, but contain more collodion-cotton, so that they are safer towards shock and useful as propellants (only slightly shattering).

The most important type is that prepared by Nobel in 1888 under the name of *ballistite* (after he had been preparing since 1878 gum dynamite by gelatinising nitroglycerine with 6 to 10 per cent. of collodion-cotton). *Ballistite* contains about 50 per cent. of nitroglycerine and 50 per cent., or even more, of collodion-cotton (with 11·2 to 11·7 per cent. N). To incorporate these two substances thoroughly and so that there is no danger in the subsequent operations, use is made of Lundholm and Sayer's process, by which the constituents are united in presence of a liquid able to dissolve neither of them. This liquid is merely water, 0·5 to 1 per cent. of aniline being added to fix the acids liberated and thus increase the stability of the ballistite.

FIG. 201.

The pulped collodion-cotton, containing 30 per cent. of water, as it comes from the centrifuges (after boiling) is introduced into a cylinder of sheet-lead containing water at 60°. The mass is well stirred by compressed air and the finely divided nitroglycerine passed in by means of a compressed-air injector. The agitation is continued until all the nitroglycerine is incorporated with the cotton, none remaining suspended in the water. The mixture is left in this condition for some weeks and is then centrifuged. It is next rolled at 40° to 50° in various machines similar to those shown in Figs. 195 and 196 on p. 241. The sheets thus obtained are then cut into strips, wires (*filite*, *cordite* [1]), cubes, granules, or shreds (*lanite*). The granulated smokeless powder thus obtained is sieved, and if in large strips these are sifted by hand; it is then placed in the drying oven, while the scraps are softened in a warm bath and again pressed. Ballistite is almost brown in colour, has a sp. gr. 1·63 to 1·65, and is practically unaffected by moisture; it inflames at 180° without exploding. The gases formed in its explosion contain no nitrous vapours and do not corrode the firearms.

With some smokeless powders, attempts have been made to replace the nitrocellulose by nitrated starch and the liquid solvents by the corresponding vapours, but no advantage has yet been procured in this way. Explosive gelatines can also be obtained by adding metallic nitrates (of barium or potassium) to collodion-cotton; these have diminished power but possess the advantage of being readily inflammable. Mixtures of collodion-cotton and nitropenta-erythritol have recently been prepared for the use of large-bore artillery.

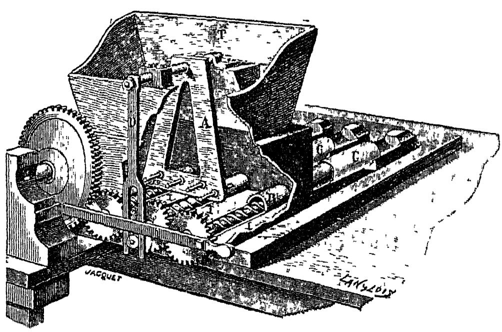


FIG. 202.

PROPERTIES OF SMOKELESS POWDERS. Those formed of nitrocellulose alone are hard; ballistite

[1] *Cordite* is a smokeless powder in filaments like hollow twine. Modern cordites contain 65 per cent. of *guncotton* (not collodion-cotton), 30 per cent. of nitroglycerine, and 5 per cent. of vaseline. Guncotton, which is insoluble (to the extent of 90 per cent.) in alcohol, ether, or even nitroglycerine, can also be gelatinised by the action of a common solvent, *e.g.* acetone, which gives a colloidal solution persisting even after evaporation of the solvent. The dry guncotton is first mixed by hand with nitroglycerine, the mass being then introduced into an ordinary kneading machine, which is of bronze and is jacketed to allow of water-cooling; the acetone (20 kilos per 100 kilos of the paste) is then added and kneading continued for at least 3 hours, after which the vaseline is mixed in for some time. The mass tends to heat and must be cooled. At the end of the operation, lumps of the paste, roughly cylindrical in form, are introduced into the cylinder of the cordite press, which is similar to that used for making macaroni. The threads of varying thickness, length, and shape of cross-section thus obtained are then dried at 40° for 5 to 8 days.

is not so hard, and even in thick strips can be bent and then broken like a very hard paste. They are very resistant to the action of water and so have a great advantage over ordinary powders, which are destroyed by water. They also possess the advantages of a high density, 1·6 or more (*see* p. 218).

Whilst Vieille's smokeless powder (gelatine of pure guncotton) withstands all ordinary conditions of temperature and moisture, ballistite, on the other hand, gradually loses nitroglycerine and so undergoes change of its properties if the humidity of the atmosphere oscillates much. But these conditions are rarely met with in practice, and ballistite is used not only by the Italian army and navy, but also by other Governments, and is in some ways superior to the cordite used in the English and also, to a certain extent, in the Italian armies. In 1906, the proportions of the components of cordite were varied slightly and the form altered to that of ribbons, being then known as *axite*. Smokeless powders withstand the blow of a projectile and require special detonators, fulminate of mercury not giving good results. They are exploded by compressed guncotton caps, which in their turn are exploded by fulminate of mercury.

If accidentally ignited, smokeless powders are not very dangerous, since they do not explode, but regard must be paid to the very high temperatures (above 3000°) produced, as these will melt iron, stone, &c.

POWDERS WITH PICRATE BASES. As early as the fifteenth century an alchemist obtained an explosive substance by treating a kind of tar with aqua regia, but this acquired no importance in comparison with ordinary gunpowder. The explosive properties of picric acid and its salts were studied in the second half of the nineteenth century and assumed considerable importance when, in 1886, Turpin prepared *melinite* from 70 per cent. of picric acid and 30 per cent. of collodion-cotton previously rendered soluble with alcohol and ether; this was regularly used for some years by the French army in place of dynamite. At the present time fused picric acid (m.pt. 122°; sp. gr. 1·6) is poured into cartridges containing a fulminate of mercury cap and powdered picric acid.

Weight for weight, picric acid is less effective than dynamite, but, measured by volume, its power is greater than that of dynamite, the specific gravity of which is 1·5. It has also the advantage over dynamite in that it does not freeze, being already in the solid state.

In England, melinite was followed in 1888 by *lyddite*, containing about 87 per cent. of picric acid, 10 per cent. of nitrobenzene, and 3 per cent. of vaseline. This is poured in a molten state into the cartridges and is exploded with ammonium picrate detonators; it is highly resistant to shock. It undergoes decomposition fairly readily, giving poisonous gases.

These and other picric acid or ammonium picrate explosives have suffered considerably in importance since the introduction of the smokeless powders described above. The properties and manufacture of picric acid will be described in the section dealing with benzene derivatives.

SPRENGEL EXPLOSIVES. In 1871 H. Sprengel, starting from the fact that explosion is nothing but instantaneous combustion, conceived the idea of preparing explosives by mixing a readily combustible substance with one possessing considerable oxidising properties; the substances separately are not explosive but become so when mixed, mixing taking place only at the spot where the explosive is to be used.

This idea was taken up later by Hellhoff, who mixed nitric acid with nitrated hydrocarbons, and more effectually by Turpin and by R. Pictet, who mixed nitrogen peroxide (N_2O_4) with various nitrated organic compounds and also with CS_2 (*panclastite, fulgurite*, &c.); but these explosives never came into practical use.

Another form of explosive of the Sprengel type is that with ammonium nitrate as base; this has been largely used during recent years and is five or six times as powerful as gunpowder.

The most important of these explosives is *Favier powder*, which, in its different forms, usually consists of a mixture of ammonium nitrate and nitronaphthalenes and sometimes contains also sodium nitrate (*see later*, Chlorate Powders).

SAFETY EXPLOSIVES (for Mines Rich in Firedamp).[1] Firedamp (*see* p. 33) is a mixture of methane and air and is formed particularly in coal-mines. It burns at 450° and inflames at 650°; in presence of spongy platinum it burns even at 200°. For ignition to occur, a certain time—at least some seconds—is necessary. For instance, at 650° about 10 seconds elapse before the explosive mixture ignites, whilst at 1000° ignition occurs in 1 second. This explains why, for example, the gases produced at a temperature of 2000° by shattering explosives do not always fire the explosive mixture, the explosion occurring with enormous rapidity (scarcely measurable). The danger of ignition is diminished by decrease of the quantity of gas formed, *i e.* of explosive used for each charge; the very hot gases produced expand rapidly and become cooled, so that they are unable to cause ignition of the firedamp. Further, if the heat of the gases is efficiently utilised to give the maximum amount of mechanical work (splitting of the rock), the risk of firing is diminished; hence follows the necessity of a good tamping for each charge in order that the escape of the gases without performing work may be prevented.

Explosion in the open is more likely to ignite firedamp. The use of a powerful detonator is advantageous, in order that the explosion may be sharp and rapid. Mine explosives should contain sufficient oxygen to produce only CO_2 and not the poisonous CO.

Instead of calculating the temperature and duration of explosion, it is preferable in practice to make direct experiments with small cannons placed against a rock at the bottom of a long, wide iron tube or *test-chamber* (20 cu. metres), containing an explosive gas. Discharge of the cannons should not ignite the gas if the explosive is safe. In France it is prescribed by law that in mines explosives must be used which give gases of maximum degree of oxidation but no inflammable gas (CO, H_2) or solid carbide: further, the calculated temperature of detonation must not exceed 1500° (or for certain piercing operations, 1900°).

Gunpowder, dynamite, and blasting gelatine readily cause explosion of firedamp in mines, their temperatures of explosion exceeding 2200° (as shown by Mallard and Le Chatelier).[2] In order to meet the requirements of a safety explosive, various ingenious processes are employed to lower the temperature of the gases from the explosion sufficiently to prevent them giving a flame. The charges are wrapped up and the tamping made with

[1] The frequent explosions occurring in mines have led scientific men during the past thirty years to make attempts to mitigate their effects and to render them less common Commissions for this purpose have been appointed in France (1880), Russia (1887), Austria (1891), and other countries In England the question has been studied by Macnab (1876) and Abel (1886), in France by Mallard and Le Chatelier (1883), Watteyne, &c, in Germany by Winckhaus (1895), very systematically by C E Bichel and Mettegang (1904–1907), who devised various ingenious forms of indicating apparatus, Beyling (1903–1907) and Heise (1898); and in Austria by Siersch (1896), Bohm (1886), Mayer (1889), and Hess (1900)

The studies of Bichel more especially have shown that the safety of an explosive for use in mines (especially coal-mines) depends simultaneously on several factors, each of which must lie within definite limits, excess of one of these not being able to compensate for deficiency of another. Thus, for example, ordinary *black powder*, which has almost all the requisites of a safety explosive, cannot be employed for the sole reason that the duration of its flame is too long and so renders it dangerous The principal factors establishing the safety of an explosive are: velocity of explosion, temperature of the gases formed, length of the flame, duration of the flame, quantity of explosive used in each explosion, &c.

[2] Dynamite and especially gunpowder, if exploded without tamping, will certainly ignite firedamp or even the coal-dust suspended in the air of coal-mines The danger is diminished but not excluded by tamping, so that even in 1853 the Englishman Elliot suggested replacing the explosives by quicklime, a large compressed charge of which is placed in a cavity in the rock, the pipe from a pressure water-pump is then introduced and a good tamping effected. The water, coming into contact with the lime, increases the volume of the latter 2 to 5 times, and, with the steam formed at the same time, pressures of 500 atmos can be obtained. In 1880 the use of lime cartridges was fairly general in mines, but they were abandoned later owing to the unsatisfactory results given. No better fortune befell cartridges of quicklime, water, and sulphuric acid, or powdered aluminium and sulphuric acid (which develop hydrogen), or chlorine and ammonia compressed separately and then united, or compressed explosive mixtures of oxygen and hydrogen. In 1876, the Englishman Macnab suggested tamping gunpowder charges with water, but this did not always prevent explosion of the firedamp; the same system applied to dynamite by Abel in 1886 gave better results. In some cases, the water is replaced by moist substances (sand, moss, &c), which yield good results.

In mines which give much coal-dust there is the greatest danger of disaster when large charges (of more than 100 to 150 grms) are used, and when the coal contains 22 to 35 per cent. of volatile products

Although firedamp ignites at 650°, explosives can be used which have a temperature of explosion only slightly below 2200° (*roburite*, 1616°; *westphalite*, 1806°; *carbonites* for coal-mines, 1820° to 1870°, &c.), since the gases cool on expanding. But even these explosives are dangerous if the charges are large (above 300 grms. for roburite and westphalite, and above 1000 grms. for the carbonites), since then a momentary pressure on the air is developed (especially if the velocity of explosion is high) and a decided rise of temperature. Explosives which, in charges of 600 to 800 grms, do not ignite the explosive mixture in the test-chamber, may be safely used in mines containing firedamp.

Ordinary black powder is, as stated above, very dangerous in such mines. More dangerous still are those explosives which cause considerable dilatation of the leaden blocks (*see later*, Fig 226, p. 262), and those which give, among their products of explosion, carbon monoxide and hydrogen but not oxygen, since these gases on burning (rapidly) withdraw oxygen from the flame of the explosive and almost stifle it A good safety explosive ceases to be such if it is not always prepared with the same care and of equal uniformity from the same materials.

water or with gelatine containing 98 per cent. of water (or with special sponges saturated with water, &c.). Salts containing much water of crystallisation have also been used for tamping, but without good results, the tamping being simply projected to a distance without evaporation of the water. A safer plan consists in mixing the explosive directly with such salts, the water of crystallisation then evaporating with considerable absorption

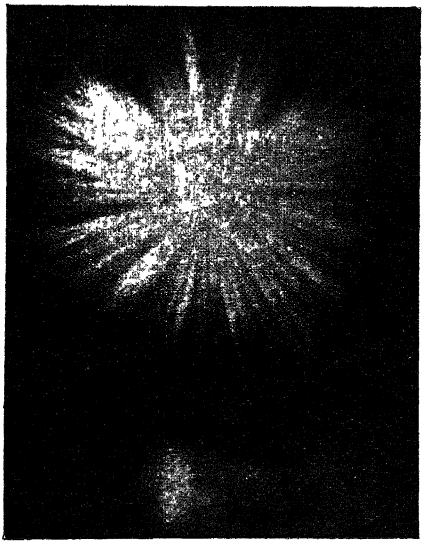


FIG. 203.

100 grms of Gelatine Dynamite

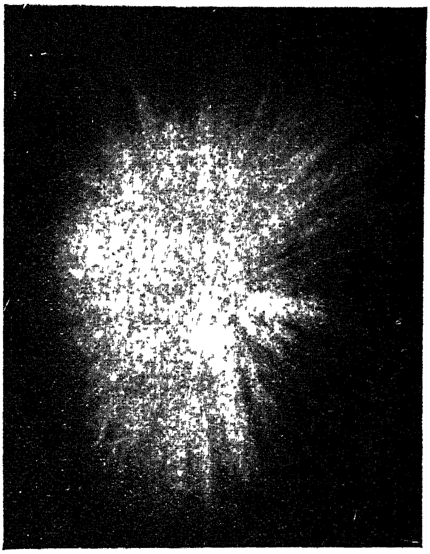


FIG. 204.

100 grms of Dynamite (Kieselguhr)

of heat, at the instant of explosion. Finally, use is made of explosives with ammonium nitrate as base, the temperature of explosion of the nitrate being only 1130° and the reaction occurring thus: $NH_4NO_3 = N_2 + 2H_2O + O$. Since, however, the explosive effect of ammonium nitrate is small, it is combined with other substances, *e.g.* with dynamite or with Favier's explosive (ammonite). In some cases, in addition to the nitrate, ammonium chloride is used, this undergoing dissociation with absorption of heat from the gases.

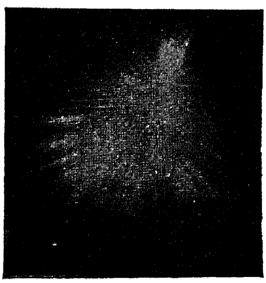


FIG. 205.

100 grms. Roburite

FIG. 206.

100 grms. Carbonite

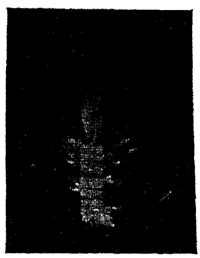


FIG. 207.

100 grms. Grisounite

Various kinds of such explosives give good results, *e.g. grisounite,* containing 44 per cent. nitroglycerine, 12 per cent. nitrocellulose, and 44 per cent. crystallised magnesium sulphate ($MgSO_4 + 7H_2O$); also *roburite,* with 82 per cent. of ammonium nitrate, and 18 per cent. of dinitrobenzene; Nobel's *wetter-dynamite,* with 53 per cent. nitroglycerine, 14·3 per cent. kieselguhr, and 32·7 per cent. magnesium sulphate; *securite,* with 37 per cent. ammonium nitrate, 34 per cent. potassium nitrate, and 29 per cent. nitrobenzene; *westphalite,* containing 94 per cent. ammonium nitrate, and 6 per cent. resin; *carbonite,* with 25 per cent.

nitroglycerine, 40 per cent. wood-meal, 30·5 per cent. potassium nitrate, 4 per cent. barium nitrate, and 0·5 per cent. sodium carbonate; *vigorite*, containing 30 per cent. nitroglycerine, 49 per cent. potassium chlorate, 7 per cent. potassium nitrate, 9 per cent. wood-pulp, and 5 per cent. magnesium carbonate. But even these substances are not safe in the absolute sense of the word; with such additions of inert products, the explosives lose in force but gain in safety.

FIG. 208.
100 grms Gelatine Dynamite, with tamping of wet paper

In 1896 Siersch, starting from the hypothesis that the smaller the flame produced in an explosion, the safer will be the explosive, photographed, on dark nights, the flames produced by the free explosion of 100-grm. cartridges. As will be seen from Figs. 203 to 208, these flames are of value although they are not absolutely decisive, since the non-luminous (ultra-violet) rays also act on the photographic plate. In Fig. 203 is seen a small luminous spot detached from the principal flame, this being due either to the surrounding gas being rendered incandescent by the shock of the explosion, or to subsequent inflaming of the gases of the explosion.

BLACK POWDER (GUNPOWDER)

This explosive, which was the first to be employed in firearms, and was the only one available for military and industrial purposes until after the middle of the nineteenth century,[1] has latterly become relatively unimportant owing to the discovery of dynamite and smokeless powders.

Ordinary black powder is a mixture of potassium nitrate, sulphur, and carbon in proportions according to the purpose for which it is required.[2]

For black military powders, used in guns and cannon in Italy, France, England, Russia, China, and the United States, the maximum power is obtained without an excessive rapidity of explosion (so as not to injure the gun too much) with 75 per cent. of potassium nitrate, 15 per cent. of carbon, and 10 per cent. of sulphur; in Germany the proportions used are 74, 16, and 10 respectively. Until a few years ago erroneous proportions were still employed, namely, 61·5, 23, and 15·5.

The chemical reactions occurring during the explosion of black powder vary according as the explosion takes place under pressure or at the ordinary pressure (deflagration). In the first case, Abel and Nobel obtained, from 1 grm. of ordinary powder, 0·585 grm. of solid products, and 0·415 grm. of gas (258 c.c.), according to the following equation: $16KNO_3 + 21C + 7S = 13CO_2 + 3CO + 5K_2CO_3 + K_2SO_4 + 2K_2S_3 + 16N$; in addition there are formed traces of potassium thiocyanate and thiosulphate, and ammonium carbonate, whilst traces of sulphur and nitre remain unchanged, as the proportions taking

[1] It is stated, but without any real confirmation, that the Chinese knew of gunpowder as early as the first century B.C., and that they used it for throwing projectiles; more certain is it that they employed mixtures of sulphur, nitre, and carbon to make rockets.

Also the ancient Indians used powders for the preparation of a kind of artificial fire. *Greek fire*, used in Greece in the seventh century, was obtained with explosive powder and probably originated in China. The Arabs were acquainted with inflammable mixtures from very remote times, whilst true gunpowder, containing sulphur, carbon, and nitre, was prepared by them only in the thirteenth century, probably after they had learnt the manufacture from the Chinese. They, however, studied its propulsive properties and constructed the first primitive guns.

In Germany it is stated that it was the monk Berthold Schwarz (a native of Freiburg, where a monument is now erected to him) who recognised the power of gunpowder in about 1320 and used it for the first time in Europe in firearms, so that the discovery, not of the powder, but of guns for throwing projectiles, is due to Schwarz. After the middle of the fourteenth century, gunpowder came into use first in Germany, then in Sweden, Russia, and elsewhere for guns and cannons. Macchiavelli records that by 1386 the Genoese and Venetians had learnt from the Germans the use of powder with guns. According to Libri, cannons were made at Florence as early as 1326. The projectiles were made first of stone, then of stone covered with iron; leaden shot began to be used in 1347, and in 1388 Ulrich Beham cast the first iron shot, which became general in the fifteenth century. The mixing of the ingredients to make the powder was first carried out by hand, and it was only in 1525, in France, that powders were graded and granulated, the mixing being effected in vertical mills like those used for expressing oil from olives.

[2] After a series of experiments in Brussels in 1560, the best proportions for the ingredients were found to be: nitre, 75 per cent.; carbon, 15·62 per cent.; and sulphur, 9·38 per cent. A thirteenth-century manuscript states that the Arabs used 74 per cent. nitre, 15 per cent. carbon, and 11 per cent. sulphur. A black powder dating from 1627 and discovered in 1905 during excavation, contained 40 per cent. nitre, 24 per cent. sulphur, and 37 per cent. carbon. In 1800 Berthollet recommended as the most effective proportions: 80 per cent. of nitre, 15 per cent. of carbon and 5 per cent. of sulphur. Berthelot has recently calculated the *theoretically* best proportions to give a maximum development of heat, his results being: 84 per cent. nitre + 8 per cent. sulphur + 8 per cent. carbon; this calculation assumes that the reagents are chemically pure, which in practice is not the case.

part in the above reaction are 77·7 nitre, 10·54 sulphur, and 11·86 carbon. With 1 grm. of powder exploded at the ordinary pressure, they obtained 0·769 grm. of the same solid products, and 0·321 grm. of gaseous products (about 193 c.c.), thus :

$$16KNO_3 + 13C + 6S = 11CO_2 + 2K_2CO_3 + 5K_2SO_4 + K_2S + 16N;$$

traces of other products are also formed, since this equation represents 82·4 per cent, nitre, 9·5 sulphur, and 8 carbon.

Sporting powder should burn more rapidly, and hence contains more nitre and a brown wood-charcoal of inferior quality. In different countries the nitre varies from 75 to 78 per cent., the carbon from 12 to 15 per cent., and the sulphur from 9 to 12 per cent. Nowadays, however, most sporting powders are of the smokeless type with a nitrocellulose base. With *mining powders* the production of a large quantity of gas is required, so that the amounts of sulphur (13 to 18 per cent.) and of carbon (14 to 21 per cent.) are increased ; if, however, the proportion of nitre is made too small, the explosion becomes very slow, more CO is produced, and the gases are partly able to escape through the fissures first produced towards the end of the explosion, the useful effect being thus diminished. Hard rocks require increased rapidity of explosion, but with tufa or granite (to obtain large blocks) greater slowness of explosion is necessary.

MANUFACTURE OF POWDER. The prime materials should be prepared with great care. The *sulphur* should contain no trace of sulphuric acid, so that stick sulphur and not flowers of sulphur is used ; if necessary, it is purified by distillation, and should yield less than 0·25 per cent. of residue on combustion. At the present time, use is also made of the sulphur recovered from soda residues (*see* vol. i, pp. 199 and 473). The *potassium nitrate* cannot be replaced by sodium nitrate, the latter being more hygroscopic and impure. The nitre should contain less than 1 part of chlorides per 3000, and should be free from perchlorates.[1] Both English nitre from India and German conversion nitre are used, after suitable purification.

The *wood charcoal* should be highly porous and should burn easily without leaving an appreciable quantity of ash ;[2] in different countries, different kinds of wood are used :

[1] For many years the superiority of English powders could not be explained, and it was attributed to the use of Indian nitre, refined in England, whilst all over Europe, *conversion* nitre, prepared in Germany, was employed On the other hand, the Germans showed that their nitre was very pure as it contained only 0 5 per cent. of chlorides, and they regarded the preference for English powder as the result of prejudice But in 1894 the elder Hellich showed that the conversion nitre contained also perchlorate, which was not shown in the estimation of the chlorides Spontaneous explosions of powder in Servia in 1896 were ascribed by Paraotovic to the use of nitre containing perchlorates. In 1897, Kelbetz showed that the perchlorate is not distributed homogeneously through the crystals of nitre, but that some of the latter contain more (and are more explosive) and others less ; hence the superiority and uniformity of powders free from perchlorate were explained. The perchlorate in nitre is estimated by Selckmann's method (1898) by fusing 5 grms. of the nitre with 20 grms. of pure lead in scales ; the fusion is first gentle for 15 minutes until the mass becomes pasty, after which the temperature is raised for a short time. The mixture of potassium nitrite, lead oxide, and chlorides is poured into water and the chlorides estimated, the excess over the amount originally present being due to the chlorates.

[2] Under similar conditions, the readiness with which powder burns is increased by increased combustibility of the charcoal. Hence it is necessary not only to use a suitable method of preparing the charcoal, but also to make careful choice of the wood to be carbonised. Light, soft wood is preferred, and of the different parts of the plant the best are branches at least three years old (5 to 8 cm. in diameter) ; the bark is rejected. For powders to be used in guns, hazel or breaking buckthorn (*Rhamnus frangula*) or hemp stalks are used, whilst for cannon and mining powders, preference is given to white willow (*Salix alba*), alder, poplar, &c. *Hemp-stalk* charcoal burns the best, and about 40 parts of it are obtained from 100 of the stalks ; hazel-wood gives only 33 per cent. of charcoal. The wood, freed from bark and well dried in the air for 2 or 3 years, still contains about 20 per cent. of moisture When heated out of contact with the air, it evolves combustible gases, but the greater part of the wood blackens without burning and forms charcoal It is of importance to determine the best conditions for carbonisation. When the temperature is not very high (280° to 340°), a light, reddish, readily combustible charcoal is obtained, whilst at higher temperatures a black, denser charcoal is obtained which burns slowly and badly, although it is a better conductor of heat and electricity.

Rapid carbonisation gives a diminished yield, but the charcoal is lighter and more friable. The charcoal is ground just before using, as in the powdered state it is much more hygroscopic and may also inflame spontaneously.

Charcoal prepared at 270° is partially soluble in caustic soda solution, whilst it is insoluble if prepared at above 330°.

Carbonisation of wood in heaps or pits is no longer employed, since the resulting charcoal is impure and non-uniform, owing to the impossibility of regulating the temperature. So that at the present time powder factories always resort to *charring by distillation*, or charring in fixed or movable *cylinders*, as proposed by the English bishop, Landloff, at the end of the eighteenth century. The distillation may be carried out in *fixed horizontal* cylinders (two to each furnace), 1 5 metre long and 0 65 metre in diameter ; but with this arrangement discharging is difficult and sometimes the heated charcoal ignites. It is better to used *fixed* vertical cylinders with openings at the bottom for emptying, or movable vertical cylinders, which can be rotated from time to time during the heating. In every cylinder, a space is left for the introduction of a pyrometer to indicate the temperature of the wood. The furnace is first heated gently, and after three hours yellowish fumes, composed of water, acetic acid, methyl alcohol, &c., begin to distil. After this, the distillation continues without further heating of the cylinder The gases are led by pipes under the hearth, where they burn at first with a bright red flame and towards the

in Spain, flax and vine stalks ; in Germany, breaking buckthorn, the alder, and the willow ; in France, the poplar, lime, &c. ; and in Italy, hemp stalks, &c. In some cases, charcoal from sugar, dextrin, maize, cork, &c., is used. Charcoal obtained at temperatures exceeding 430° is of no use for gunpowder.

PULVERISATION AND MIXING OF THE INGREDIENTS. In early times the ingredients were ground and mixed by hand in mortars, but machine mills were used as early as 1350. In the seventeenth century, the use of wooden stamps became widespread, but these were the cause of many explosions, so that the vertical mills again came into use, the powder being kept moistened with water during grinding. At the present time the ingredients are powdered separately, then partial mixtures of sulphur and charcoal, and charcoal and nitre, are made, these being finally united and intimately mixed. The finer the materials are powdered the better will be the resulting powder.

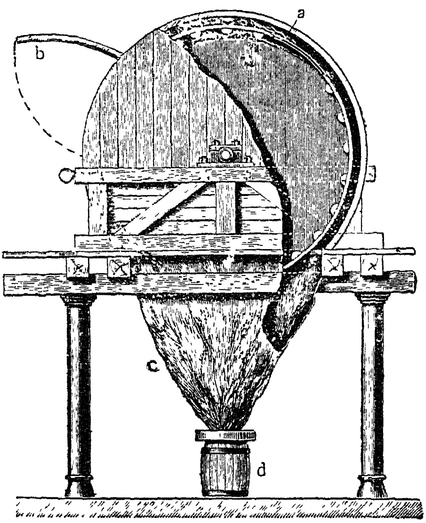


FIG. 209.

The charcoal and the sulphur may be powdered in the Excelsior mill (*see* p. 168, Fig. 162), the product then being sieved and the coarse particles reground. The nitre is received from the refiner in the form of flour and only requires sieving.

The *binary mixtures* are prepared by placing the powdered substances in special iron drums (Fig. 209), 1·1 to 1·2 metre in diameter, and 0·6 to 1·2 metre long. On the inner periphery of the drum are 12 to 16 transverse ribs, 3 to 4 cm. thick. Hard phosphor-bronze balls, 15 to 20 mm. in diameter, are introduced with the two substances through the aperture *a*, which corresponds with the hinged cover *b*, fixed on the cylindrical wooden casing surrounding the drum. This wooden casing is connected with a leather or cloth bag, *c*, by which the mixture is finally discharged into the barrels, *d*, these being closed hermetically so as to prevent contact with the air, which might cause ignition (*see* vol. i, Pyrophoric Substances).

The drum is rotated about 15 to 20 times per minute for 8 to 10 hours, 100 to 150 kilos of the bronze balls being used per 200 kilos of the mixed substances ; the balls are given a bumping motion by the peripheral ribs and so increase the fineness of the powder. When the aperture, *a*, furnished with a coarse net, is opened at the end, the powder is discharged and the balls retained for a subsequent operation (*see also* the figures of ball mills, vol. i, p. 512).

The *ternary mixture* is prepared by mixing either binary mixture with the third constituent or the two binary mixtures (carbon + sulphur, and carbon + nitre) in the required proportions in a rotating cylinder provided with stirrers, or, better, in a drum similar to that just described. After this the mass is moistened with water and mixed, and then introduced into a stamp mill (like that shown in vol. i, p. 514), where it is kept moistened (with about 10 per cent. of moisture) without caking. The stamps make 30 to 60 blows per minute, and their action is continued for at least 12 hours for cannon powder, 8 hours for mining powder, and 24 hours for sporting powder. The cakes thus obtained then pass to the granulating machine.

In many factories, however, the use of stamps has been abandoned, these being replaced

end of the distillation with a bluish red flame. When the distillation is finished, the cover of the cylinder is raised and the charcoal discharged into suitable movable cylinders, which are immediately closed to exclude the air. Into the cylinder, while still hot, another charge of wood is at once introduced. Each charring lasts at least 10 hours. In three or four days the charcoal is cold and is then removed lump by lump from the cooling cylinders, any that is insufficiently burnt being rejected. The colour of the charcoal is coffee-black, the fracture being velvety and of the same colour.

An improved process of distilling wood by means of superheated steam, proposed by Violette in 1847 and perfected by Gossart in 1855, was abandoned on account of its excessive cost.

In 1899, H. Guttler in Germany suggested the replacement of the superheated steam by hot carbon dioxide in order to obtain a rapid charring; after the operation, the mass can be quickly cooled by a current of cold carbon dioxide.

by vertical iron runners (Fig. 210) about 1·6 metre in diameter and 40 cm. thick, and weighing about 5000 kilos each. They rotate on a very hard iron plate 2 metres in diameter. The two runners are placed at different distances from the central shaft, which is actuated by bevel wheels above (as in the figure) or below; suitable scrapers detach the powder sticking to the runners, and others bring the powder from the edge to the centre and so under the runners. This incorporation is continued for 3 hours in the case of military powder and for 5 hours with sporting powder, the velocity of the runners being 10 to 12 revolutions per minute at first and only 1 revolution in 20 minutes towards the end of the operation, so that highly compressed cakes may be obtained. About every hour the mass is moistened with 1 to 1·5 litre of distilled water for a charge of 20 kilos, the amount of water used depending on the hygrometric state and temperature of the air. The water dissolves the nitre, which is thus distributed uniformly and in a finely divided state throughout the whole mass.

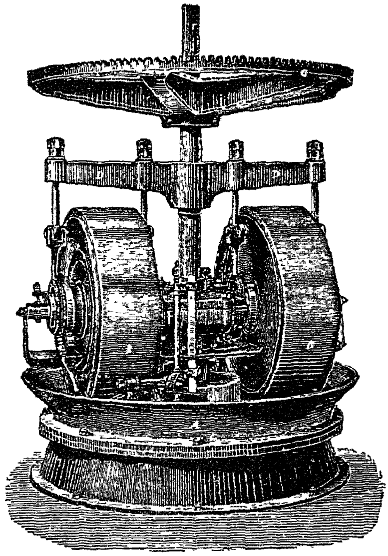


FIG. 210.

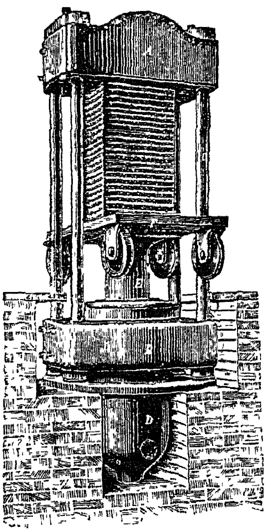


FIG. 211.

In some factories, compression of the moistened ternary mixture is effected by means of *hydraulic presses* (Fig. 211) between a number of separate layers of copper or ebonite, a pressure of 100 atmos. being applied for three-quarters of an hour. This procedure yields very compact cakes, having the density 1·7 to 1·8.

It was formerly the custom in France, and is still in Germany, to use *roller-presses* (*laminoirs*) (Fig. 212) formed of three superposed rolls; the lowest one, *C*, of cast-iron, is driven directly and transmits the movement to the middle one, *B*, which is coated with paper; this then drives the uppermost one, *A*, of chilled cast-iron. The endless band, *D*, collects the mixture falling from the hopper, *E*, and carries it between *B* and *A*, between which a pressure of 15 to 25 tons can easily be obtained by means of the lever, *L*, and weights, *P*. A knife is arranged so as to scrape the compressed powder from the band.

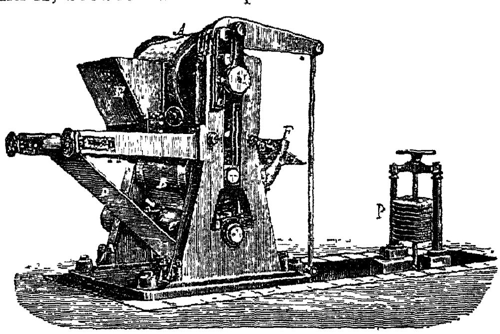


FIG 212.

As a rule, moist compression gives a more uniform and also a denser mass.

After compression the cakes still contain 5 to 8 per cent of moisture, and they are allowed to stand for 7 to 8 days in well-ventilated magazines. After this, those from the hydraulic presses or roller-presses are first dried (*see later*) and then granulated, whilst those from the stamps or incorporating mills, being less moist, are granulated directly.

GRANULATION. This operation serves the purpose of preventing the separation of the constituents, and of rendering the powder less hygroscopic and less compact (but not less dense), since the combustion of the granules is more rapid than that of the fine compact powder; also, the finer the granulation the more rapid is the combustion and the greater the mechanical effect. The finest grains are used for sporting powders, then

come those for military rifles, the coarsest grains being for cannon. If sporting powder were used for military rifles, the barrel would wear out rapidly and might even split.

It was only after 1445 that powder for artillery was granulated, it being found that the effect was greater than that of the non-granulated and non-compressed powder. Compression with stamps or rolls came into general use in France after 1525, the compressed mass being then broken up with wooden hammers and granulated ; for this purpose, the mass was spread out on a large sieve and covered with a heavy disc of wood, the sieve being then rotated and oscillated until all the powder passed through it in grains.

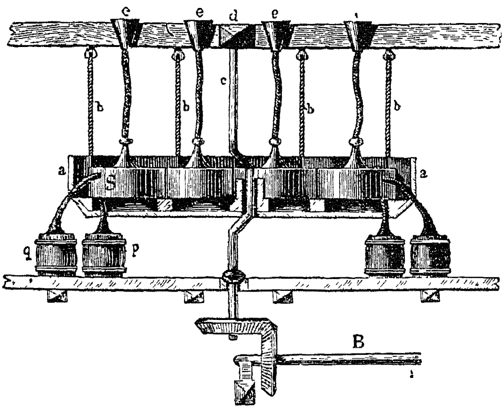


FIG. 213.

Later the *Lefèvre graining* machine was devised, and this is still in use in France and Germany ; this machine grades the grains into different sizes and also eliminates all dust, powders showing more regular and rapid combustion being thus obtained.

This machine (Figs 213 and 214) consists of an octagonal board with sides, *a*, having a diameter of 2·5 metres and suspended from the ceiling by 8 ropes, *b*. This receives a circular motion by means of an eccentric formed of a vertical shaft, *c*, with an elbow-joint. This shaft is rotated at the rate of 75 revolutions per minute by the cog-wheels, *B*. On the board are fixed 8 or 10 triple sieves, *S*, to which the powder to be granulated is supplied by leather or cloth tubes, *e*. The powder falls on to the first wooden sieve, *A* (Fig. 214), with a mesh of 3 to 4 mm., the coarse lumps being gradually broken by a disc of wood, *c*, weighing 700 grms. The grains then pass on to a second sieve, *B*, of metal, 3 to 4 cm. below, and then to the lowest one, *C*, which is of hair and retains the grains of the required size, whilst the dust falls into *D* and thence through the leather pipe, *g*, into the barrel, *p* ; the uniformly grained powder is discharged into *q* through *f*.

More common at the present time is the granulating machine with fluted rolls, first suggested in 1819 by the Englishman, Colonel Congreve, and subsequently improved in various ways. This machine (Fig. 215) consists of several pairs of bronze rolls, *A*, *B*, *C*, fluted longitudinally and transversely. The lumps of powder from the breaker, *F*, are raised to *E* by an endless band, and fall on to the first rolls, *A*, furnished with small pyramidal teeth projecting 10 mm., then on to the second rolls, *B*, with finer teeth (3 mm.), and finally on to the smooth rolls, *C*, which give the powder the appearance of shining scales. The distance between the rolls is adjustable, and the teeth are kept clean by means of a brush. The granulated powder falls on to a series of superposed sieves, *S*, which are oscillated at the rate of 150 vibrations per minute, and so grade the powder, the final dust being discharged at *m*. Blasting powder, which has the size of peas, is not passed through the smooth rolls. By varying the mesh of the sieves, grains of any desired magnitude are obtainable. Congreve's granulating machine gives a yield four or five times as great as that of Lefèvre (for the same consumption of power) and also forms less dust.

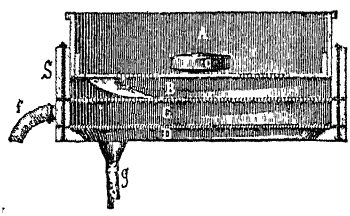


FIG. 214.

DRYING. The granulated powder is sometimes dried by spreading it out in layers 5 cm. deep on cement floors exposed to the air and sun and mixing it occasionally with rakes ; this drying is continued until the moisture is reduced to 3 per cent.

Artificial drying, which is independent of climatic conditions, is, however, more commonly used. In early times the powder was placed in copper pans heated directly over the fire, but this led to many explosions ; later it was spread out on cloths in a chamber heated by a stove in the centre, but this also was dangerous even when the stove was

outside the chamber. Nowadays drying is generally effected by air (used for the first time in England in 1780) which is heated by a network of steam-pipes and is injected into a drying-room containing the powder spread on cloth in layers 5 to 15 cm. deep, mixing with wooden rakes being resorted to about every two hours. The air passes through the powder and is carried off by flues; the drying takes 8 to 10 hours. The fire of the steam-boiler is at least 100 metres from the drying-room.

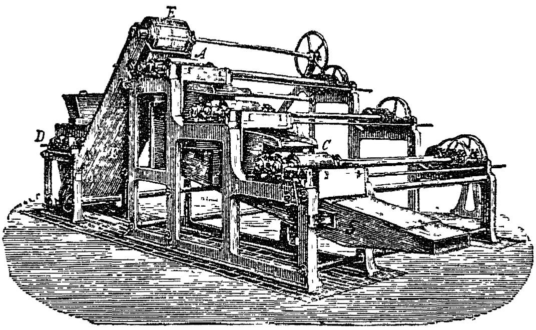


FIG. 215.

Dry powder can be powdered between the fingers, giving a pale, grey powder, but if not dry it is dark and sticks to the hands. In some factories the air used is previously dried (and is employed cold if the nitre present tends to effloresce, but hot in other cases) by being forced with a fan, *A*, (Fig. 216), through fused, spongy calcium chloride or concentrated sulphuric acid contained in a leaden vessel, *D*. Thence it passes into the chest, *E*, filled with lumps of quicklime, which holds back any acid carried over. It is then heated in the brickwork chamber, *B*, by a number of pipes, *c*, supplied with steam at *d*; the warm, dry air then proceeds through the tube, *V*, to the drying-rooms.

The proposal has also been made to dry powder by heating it in a vacuum, but such a process is too costly and its efficiency low. Drying need not be complete, since the powder has still to be glazed.

GLAZING. The dried grains are rough, angular, and highly porous. In order to give a brighter appearance to the powder and to render it more uniform and dense and less hygroscopic, it is treated in wooden glazing drums (*Champy drums*, similar to those used for the binary mixtures; *see above*) after having been passed through a fine sieve to free it from adherent dust. The inner walls of the drum are first moistened and the drum slowly rotated while the powder is being introduced until about 300 kilos are present, the velocity being then raised to 12 to 14 revolutions per minute; the finer the granulation the more rapid must be the rotation. In this way the powder becomes heated to about 50° and assumes a gloss; care must, however, be taken that it does not become too hot, and towards the end of the glazing the rotation must be slackened. A little graphite is sometimes added (0·25 per cent.) to render the powder less hygroscopic and more glossy. Glazing takes 4 to 5 hours for blasting powders and 15 to 20 hours for sporting powder.

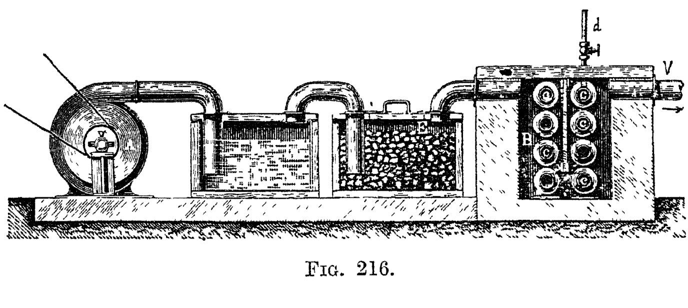


FIG. 216.

Glazing is due to the rubbing of the grains one against the other. The powder is subsequently dried completely in the usual drying-rooms, or the panels of the drum may be opened so as to allow of the escape of the warm, moist air.

Polishing and *sorting* are carried out, after the glazing and drying, to remove the last traces of dust and separate the different sizes of grains. For these purposes a battery of sieves similar to those of the Lefèvre and Congreve graining machines is used, the sieving being repeated several times. The dust contains about 75 per cent. of carbon.

PRISMATIC POWDER FOR CANNON. It was shown by San Roberto as early as 1852 that cannon give better results if charged with compressed cartridges of regular form; and the American, General Rodman, proposed in 1860 to make large grains of regular shape. The use of such powder was extended in Russia, by General Doremus, and also in other countries, but was found to give better results for blasting than for military powder. In

England, Armstrong's grains, in the form of hazel-nuts, met with great success and are still used. In 1879, by means of special hydraulic presses (cam-presses), Wischnegradsky prepared the first prismatic powders, six or seven holes being left in each prism (Fig. 217) to diminish the initial pressure on the cannon and give a more regular combustion. Every prism is 25 mm high and 40 mm. in diameter, and weighs 40 grms.; it has the density 1·66 and bears the mark C.66. It is used for 15 to 26 mm. guns, whilst that for larger cannon has the same volume but the sp. gr. 1 75 (marked C.75). The brown prismatic powder of Rottweil of Hamburg has the sp. gr. 1 86 (C 86), and is used for large cannon, since it burns slowly, gives little smoke, and keeps well; it is prepared with rye-straw charcoal and contains 78 per cent. of nitre, 3 per cent. of sulphur, and 19 per cent. of brown charcoal.

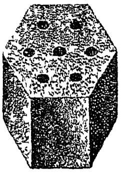


FIG. 217.

PACKING. Powder is packed in bags containing from 50 kilos, these being placed in barrels or cases coated inside with paper and outside with cloth. Each case bears a label of a colour indicating the nature of the powder (rifle, cannon, &c.). Sporting powder is placed in tin boxes holding 100, 200, 500, 1000, or 2000 grms., these being then arranged in cases containing 25 kilos.

Powder for firing volleys or ball is converted directly into cartridges, which are then stored in cases in sawdust, cotton waste, or similar packing.

CHARACTERS AND PROPERTIES OF BLACK POWDER. It has a slate-grey colour, and, if too black, either it is damp or it contains too much charcoal. Certain military powders have a brown colour, as they are prepared with reddish brown charcoal. If rubbed on a sheet of paper it should not leave a dirty mark, as, if it does, it contains dust or moisture. When a small heap of powder is ignited on a sheet of white paper it should burn rapidly without leaving a residue or burning the paper; if very black spots remain, there is excess of charcoal, or if yellow ones, excess of sulphur. On exposure to the air, good powder absorbs only 1·5 to 2 per cent. of moisture, whilst as much as 14 per cent. may be absorbed by inferior powder. If the moisture-content of powder is only 5 per cent. it can be removed without damage to the powder, but moister powders cannot be restored to their original strength by drying, since the grains become covered with a crust of nitre. The finer the powder and the richer in charcoal, the more hygroscopic it is.

The temperatures of ignition and explosion are the same, and ignition or explosion can be produced by red-hot iron or any ignited substance, or with less ease by percussion, shock, or discharge. It is more difficult to ignite by a blow of iron on copper or copper on copper than by one of iron on iron or brass, or of brass on brass, &c. Powder ignites more readily by a spark or red-hot body than by a gas-flame. Guncotton burns on powder without igniting it. Different powders ignite between 270° and 320° according to the form of the granulation.

VARIOUS POWDERS. During recent years there has been very keen rivalry between different makers to prepare new powders for special purposes (even for shooting pigeons !), and also blasting powders more economical than black powder. For powders to be used immediately or stored in very dry magazines, the potassium nitrate is replaced by *sodium nitrate* (although this is more hygroscopic) which is cheaper and gives a larger proportion of oxygen; the charcoal has also been partially replaced by other organic substances (tar, sawdust, flour, and even horsedung). These powders, often short-lived, are given most extravagant names (*violette, gunn, fulopite, pyrolite, pudrolite,* &c.).

Chlorate powders, first proposed by Berthollet in 1785 to obtain greater power and containing potassium chlorate instead of nitre, have not been very successful, and even when a part of the nitre is restored, accidental explosions often occur owing to the great sensitiveness to shock. In America, Devine (in 1881) retains the potassium chlorate but keeps the ingredients of the powder separate until required (as is done with the Sprengel explosives, p. 245); thus *rackarock* for blasting contains 79 per cent. of potassium chlorate and 21 per cent. of nitrobenzene (liquid) mixed sometimes with picric acid, sulphur, &c. These powders are rendered less sensitive to shock by mixing with a little wax (*e.g.*

Brank's powder). In 1896, at St. Petersburg, Jevler prepared *promethus* from a solid portion (potassium chlorate + manganese dioxide + ferric oxide), and a liquid portion (mononitrobenzene + turpentine oil + naphtha); a factory for this explosive was erected in Italy in 1905, but it was destroyed by a terrific explosion in 1909, ten persons being wounded and five killed. In 1901 *donnar* was placed on the market; it contains 56 per cent. of chlorate and 24 per cent. of potassium permanganate for the solid part, and 16 per cent. of nitrobenzene and 4 per cent. of turpentine for the liquid part. Also nitronaphthalene and castor oil (5 to 8 per cent.) are used to render the mixture more stable, *e.g.* with *cheddite* and with *pierrite*: 80 per cent. of chlorate + 12 per cent. nitronaphthalene + 6 per cent. castor oil + 2 per cent. picric acid (or, better, 2 per cent. dinitrotoluene), the whole being well mixed; this powder has double the power of ordinary blasting powder.

More advantageous still are thought to be the *potassium perchlorate powders* (*Nisser* powder, 1865, contains: perchlorate, 10·5; nitrate, 44·5; bichromate, 2; ferrocyanide, 1·5; sulphur, 15·5; charcoal, 19·5; and vegetable substances, 6·5 per cent.). Better still are those containing *ammonium perchlorate*, recently invented by U. Alvisi (*manlianite*: 72 per cent. perchlorate, 14·75 charcoal, 13·25 sulphur; *Cannel powder*: 80 per cent. of perchlorate and 20 per cent. of cannel coal; *cremonite*, with 48·85 per cent. of ammonium perchlorate, and 51·15 per cent. of ammonium picrate; and the *kratites* obtained by mixing perchlorates with nitroglycerine and with nitrocellulose). Perchlorate powders should be used cautiously, and to render them less sensitive without impairing their great shattering power, they are mixed with urea, guanidine, dicyanodiamidine, &c.; if nitrate is added, the chlorine is fixed, and the explosions then obtained are especially suited to mines with thin and extended seams.

In 1905 a patent was taken out for a powder containing 47 per cent. of ammonium nitrate, 1 per cent. of charcoal, 30 per cent. of orthonitrotoluene, and 20 per cent. of very finely powdered aluminium, the whole being compressed under a pressure of 5000 kilos per square centimetre, and then moistened with nitrotoluene in a water-bath at 67°.

DETONATORS (Caps, Fuses). Detonators serve to produce explosion of explosive substances. For black powders it is sufficient to produce a spark in the mass by means of a heated fuse, but with nitroglycerine or guncotton explosives, neither the fuse nor the black powder causes explosion, ignition being the most they produce. In these cases use is made of fulminate of mercury, which explodes by simple percussion or heat, and produces an explosive wave capable of inducing the explosion of these explosives. Moist or paraffined compressed guncotton requires more powerful caps of dry guncotton, these being then exploded by fulminate of mercury detonators.

FULMINATE OF MERCURY, $(C:N\cdot O)_2Hg$, the composition and constitution of which are given later (*see* Fulminic Acid), was discovered by Howard in 1799 and studied as regards its constitution by Gay-Lussac, Liebig, Gerhardt, Kekulé, &c. Its manufacture requires great care and exact proportions of the reagents. So long as fulminate of mercury is moist it presents no danger, but it must be handled with extreme care when dry.

It is best prepared by Chandelon's process: into a glass vessel of about 4 litres capacity are placed 100 grms. of mercury, to which are added 1000 grms. of nitric acid of 40° Bé. (sp. gr. 1·383), the liquid being stirred until all the mercury is dissolved. The greenish liquid is allowed to cool to about 20° and is then poured into a flask of at least 5 litres capacity containing 635 grms. of 90 per cent. alcohol; bumping or fuming of the liquid is of no consequence. Very soon the liquid begins to boil spontaneously, to become decolorised and to evolve gas and white poisonous vapours (CO, ethyl nitrate and acetate), and then yellow vapours of nitrogen peroxide.

The mass darkens slightly, and when the maximum fuming occurs, 80 grms. of 90 per cent. alcohol are added a little at a time, and then a further quantity of 55 grms. of alcohol, the boiling being thus somewhat attenuated. After it has been left until the white vapours have disappeared, there appears on the bottom a voluminous whitish powder, which is the fulminate of mercury. The operation lasts altogether 15 to 20 minutes and should be carried out under a hood with a strong draught, or else the flask should be fitted with a stopper and wide delivery tube to carry the vapours to a flue. The product is poured on to a filter, washed 10 to 15 times with water—until the wash-water no longer shows an acid reaction [1]—and the filter with the fulminate spread out on other

[1] The filtrate and the wash-water are utilised by first neutralising with milk of lime or calcium sulphide (or by decomposing with hydrochloric acid); from the precipitate the mercury is recovered, whilst witherite is added to the liquid to form barium nitrate, the alcohol is recovered by distillation.

absorbent paper in the air (not in the sun) until it is dry (about 10 per cent. of moisture remaining). To dry it completely and safely, vacuum drying-ovens at a temperature below 40° are now used.

Theoretically 100 grms. of mercury should yield 142 grms. of the fulminate, but practically about 125 to 128 grms. are obtained. In the dry state, it is sold at 9*s.* 6*d.* to 12*s.* per kilo ; when not used at once, it is stored under water. If necessary, it can be purified by dissolving in hot water (solubility 1 : 130), from which it crystallises on cooling. It is whitish or sometimes faintly yellow (if a small quantity of HCl or NaCl is added to the nitric acid used in its manufacture, white crystals are obtained), poisonous and soluble in alcohol.[1]

It has an extraordinary shattering power owing to its very great rapidity of explosion. It is exploded by a blow or by brisk rubbing, and gives a pressure of 27,400 atmos. When

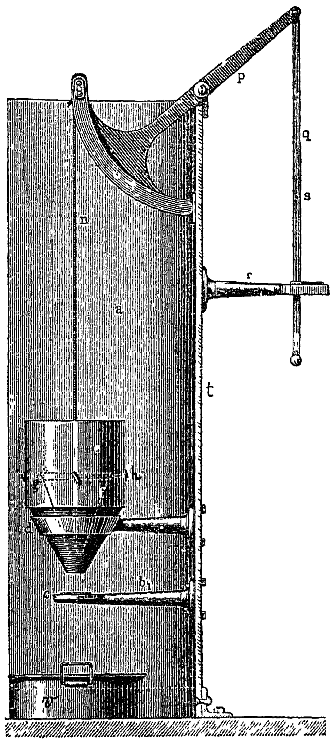


FIG. 218.

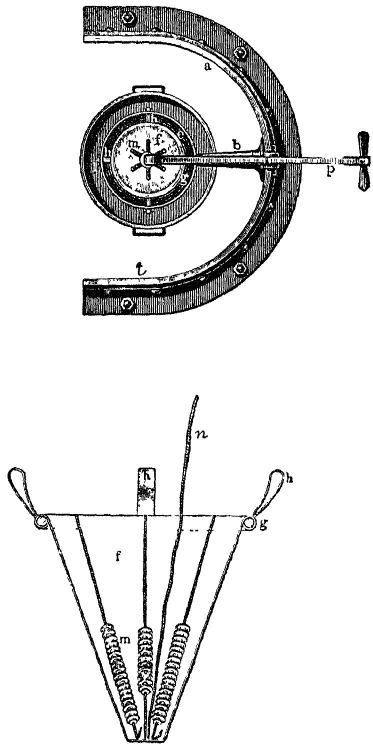


FIG. 219.

heated slowly it explodes at 152°. All objects used in its manipulation must be of wood, not of iron. Since it is scarcely ever used alone for preparing caps, but is mixed with an equal weight of potassium chlorate and about 25 per cent. of antimony sulphide, it is sometimes, in order to avoid explosion, made into a paste with a thick solution of gum, the required quantity being poured into each copper cap (which contain about 15 or 20 mgrms. of fulminate for sporting caps or 1 to 1·5 grm. for caps to be used with dynamite cartridges), these being then very carefully dried in vacuum drying ovens. When, however, these mixtures are prepared in the dry state, in order to prevent explosion the mixing is carried out in the apparatus shown in Figs. 218 and 219. In a leather box, *e*, a leather bag, *f* (the so-called "jelly-bag") is suspended by the loops *h*, attached to the gutta-percha ring, *g*. To the bottom of the bag and to the ring, *g*, are joined several cords on which are threaded rubber rings, alternately large and small. Another cord, *n*, attached

[1] Analysis of Fulminate of Mercury (Brownsdon's method): the fulminate is first purified by dissolving it in potassium cyanide and reprecipitating it with dilute nitric acid ; it is filtered, carefully dried, and a weighed quantity of 0·04 to 0·05 grm. dissolved in 30 c.c. of water. One gramme of thiosulphate is then added and the liquid shaken and made up to 100 c.c. with water. The free alkali in 25 c.c. of this solution is then estimated by titration with N/10-sulphuric acid in presence of methyl orange as indicator.

to the lever, $p\ q\ s$, admits of the bottom of the bag being raised and lowered so as to mix the ingredients. When mixing is complete the bottom of the bag is drawn completely up, so that the contents fall into the space between the bag and the box and thence into the collecting vessel, v.

The workman is protected from the effects of a possible explosion during the operation by a semi-cylindrical wrought-iron screen, t. The caps are then very carefully charged by compressing the mixture with a suitable machine or press, which gives a pressure rising gradually to 260 atmos. (pure fulminate will stand 7000 atmos. without exploding, but in presence of other substances, *e.g.* sand or coke powder, or other hard body, it will explode with a very small pressure). During the charging the operative is always sheltered by iron screens.

In general, no attempt is made to economise in detonators, since the explosion has a greater and more complete effect if the detonator produces the maximum initial violence.

The explosion of detonators or caps, and hence of the cartridges or charges of explosive, both in blasting and military operations, is effected electrically or with fuses.

Fuses should burn with a definite velocity so as to allow the miners to reach a place of safety before the explosion. This requirement is satisfied by the *Bickford fuses* (devised in 1831 by the Englishman, Bickford). These consist of a compact cord prepared in a

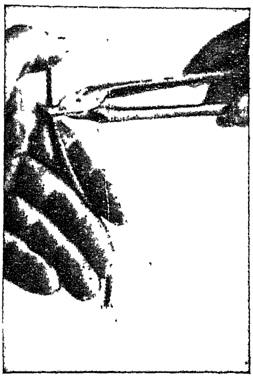


FIG. 220.

FIG 221.

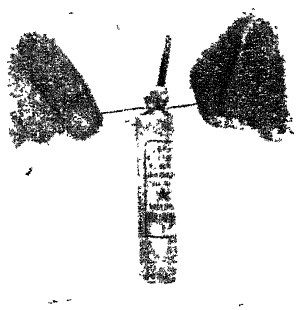


FIG. 222.

special manner from jute or cotton threads, which are spun round one another in opposite directions and are rendered impermeable by tar or gutta-percha. These fuses or cords, 5 mm. thick, have an empty central core, which is then filled with finely granulated, compressed powder. They then burn with a velocity of 1 metre in 90 seconds. To explode black powder, it is sufficient to fix the fuse into the mass of the charge, which explodes as soon as the flame reaches it.

For dynamite, gelatine dynamite, and explosive gums or gelatines, use is made of a fulminate of mercury detonator which explodes a dynamite cartridge, this then causing explosion of all the other cartridges (without caps) surrounding it. The fuse is cut clean and introduced into the bottom of the copper cap containing the fulminate, and is fixed to the cap by squeezing it with suitable pincers (Fig. 220). The parchment paper at one extremity of the cartridge is then opened and the cap thrust into the cavity left for it (Fig. 221), the paper being then tied tightly round the fuse with string so that the cap and fuse cannot become detached from the cartridge (Fig. 222).

Ordinary fuses, which are very irregular, are obtained by soaking soft cotton cord with lead or potassium nitrate ; such fuses must be well dried before use, as they are hygroscopic. The cord may also be impregnated with a paste of gum and fine black powder and then dried. Almost instantaneous fuses may be made from guncotton.

The importance of tamping after the introduction of the cap into the charge has already been mentioned.

Electric fuses are used, especially for dynamite and fulminate caps, and serve well for producing the simultaneous explosion of several charges, this giving a greater effect than separate explosions ; they are also useful in galleries which contain firedamp, as the

latter would be exploded by a burning fuse. A spiral of thin platinum wire is fixed in contact with a little dry guncotton above the fulminate of the cap. The two ends of the wire are connected separately with two insulated wires joined to a small battery, accumulator, or hand dynamo, which heats the wire and so causes explosion. Use is often conveniently (since the fragile platinum spiral is eliminated) made of an electric spark formed between two platinum points very near to one another in a mixture of potassium chlorate and antimony sulphide contained in the cap ; in this case the sparking is effected by a device similar to a Leyden jar (*Bornhardt exploder*) which gives a high-tension current, or by one utilising induced currents (*Bréguet exploder*) ; these can be placed at a distance from the charge by lengthening the conducting wires.

DESTRUCTION OF EXPLOSIVES. In various cases it is necessary to destroy explosives, when these have altered or undergone partial decomposition, or when residues are left from samples submitted for analysis. With black powder it is sufficient to immerse it in water and so dissolve out all the nitre, and then to burn the barely dry insoluble residue. Water does not, however, destroy nitroglycerine or the various dynamites ; with these the caps are carefully removed and also the wrapper (including the parchment paper), the cartridges being placed in contact one with the other on a long strip of paper in a field free from stones and away from any building ; they are then sprinkled with petroleum and a long fuse, attached to the first cartridge, lighted. In this way the cartridges burn without exploding. With frozen dynamite cartridges which have undergone change, it is dangerous to handle them, and they must be very carefully exploded one by one in the open with a fulminate cap and fuse. Nitroglycerine can be made into a paste with sawdust and burnt as described above. Small quantities of explosives may be burnt in pieces the size of a pea, and small dynamite residues may be decomposed by heating on a water-bath and frequently stirring with concentrated alcoholic caustic soda solution.

STORAGE AND CARRIAGE OF EXPLOSIVES. Explosive factories are placed at a distance of about 1000 metres from any dwelling-house or frequented street. The ideas underlying the construction of magazines are very varied. In some countries (Austria, Italy, France, and, in part, Germany), the prepared explosives are distributed in a number of small magazines far from the factory, and constructed of wood so as to minimise the danger from projection in case of explosion ; they are separated by large mounds of earth as high as the magazine, so that the explosive wave or projected material may not reach neighbouring magazines. Also in some magazines a kind of wide bridge covered with earth is constructed over the magazine to annul or attenuate the effect of projectiles falling from above. In England, however, it is assumed that, owing to the perfection of the systems of manufacture and of chemical and physical control of explosives, explosion is not to be regarded as possible, so that large, very solid magazines are built, either wholly of cement or partly of iron, the walls being half a metre thick. The distance between the separate magazines varies from 100 to 200 metres, according as the amount of explosives stored is more than 2000 or 10,000 kilos. The flooring is of wood, and the magazines are heated in winter by means of steam-pipes in order to prevent freezing of the explosives. In general there are no windows, but only double doors and small apertures ; artificial illumination, which is rarely used, consists of lamps placed outside the apertures or electric lamps hermetically sealed with gutta-percha and fitted with several glass coverings ; in some cases the electric lamps are immersed in water.

Any person entering a magazine must wear felt slippers or leather boots without nails. The most serious danger is not that of accidental explosion but that of lightning. When storms threaten all work is suspended, while the magazines are protected from lightning by all the most modern appliances.[1] Even the methods of packing explosives and loading

[1] In general the protection afforded by lightning conductors is due to the fact that lightning is rendered harmless if it meets good and sufficiently extensive conductors of electricity. There is, however, always great danger if inside or outside the buildings protected there are large masses of good conducting materials, such as the iron and lead pipes of dynamite factories, as these may cause deflection of the lightning even from its path in the lightning conductors.

At the Nobel dynamite factory at Krummel on the Elbe, there was a great explosion in 1900, lightning striking the iron compressed-air pipe and being thus led to the vessels full of nitroglycerine, which consequently exploded.

Franklin's principle, according to which a metal rod furnished with points should serve to discharge to earth the large electric charges of the clouds, is not applicable to the protection of explosive factories, since such rods on factories do not discharge the clouds to a sensible extent, but can only serve to conduct the lightning to earth after the shock. Much more rational is Faraday's method of attempting to discharge the electricity of the clouds or to conduct the lightning by so many metallic wires as to prevent it from subdividing, no secondary circuits which might produce sparks being, however, formed. According to Faraday, the most certain protection against lightning consists of a metal cage surrounding or covering the building to be protected, and many military explosives

them on waggons for transport are subject to detailed regulations: by legislation dating from 1875 in England and from 1905 and 1909 in Germany, and in Italy by a series of laws and regulations of various dates. In every case, a despatch must be preceded by a permit and by a warning to all the stations on the route. Explosives are despatched only on certain days and in certain trains. In Germany, chlorate and perchlorate travel without restrictions. Owing to the great stability of modern explosives, only 6 out of 265 accidents due to explosives occurred during transport.

ANALYSIS OF EXPLOSIVES. The quantitative determination of the components of black powder is comparatively simple: 10 to 20 grms. of the sample are dried in an oven until constant in weight (*moisture*) and are then extracted with hot water, which dissolves the *nitre*, this being weighed or analysed separately. From the dried residue the *sulphur* is extracted by carbon disulphide in a Soxhlet extraction apparatus. The residue then contains the charcoal, graphite, and any impurities (sawdust, mineral carbon, &c.) which can be identified under the microscope. The density of the powder is determined by means of a *densimeter*, and the size of the grains and the quantity of dust by suitable sieves.

The *analysis of dynamites* and of smokeless powders is more complicated and must be carried out with great care. In *dynamites with inert bases* the proportions of nitroglycerine, moisture, and inert substance are determined: 8 to 10 grms. of the dynamite, cut into pieces the size of peas, with a wooden or bone spatula, are weighed on a clock-glass and left in a desiccator over calcium chloride (not sulphuric acid) for some days until of constant weight: the loss in weight gives the *moisture*. The dried mass is extracted with pure dry ether free from alcohol, in a Soxhlet apparatus (as in the extraction of fat, *which see*), the heating being effected with water at 50° to 60° and the ether subsequently distilled with water at 40° to 50° away from the neighbourhood of a flame. The nitroglycerine becomes turbid when almost all the ether is evaporated, but clear again when the evaporation is complete; the *nitroglycerine* is dried until constant in weight in a vacuum desiccator over calcium chloride. The residue left in the extractor (*kieselguhr* or other inert matter) is dried at 60° to 70° and weighed. It is sometimes sufficient to determine the nitroglycerine by difference from the weight of this residue; the result is exact enough and the operation more rapid and less dangerous.

Dynamites with *active bases* sometimes have complex compositions and the analysis is not always so easy[1]; in general, the nitroglycerine and collodion-cotton are separated from the residue by alcohol and ether, from which the collodion-cotton is precipitated with chloroform.

stores are effectually protected in this manner. In 1900, Professor Weber proposed the protection of the Krummel explosives factory by fixing to iron columns galvanised wire-netting (88 meshes per sq metre) furnished with metal points so as to form a kind of roof a metre or more above the factory.

The columns are also provided at the top with metal points and serve to conduct the electric discharge to the earth. In the wires forming the network sharp curves are avoided in order to facilitate conduction and hinder any divergence of the lightning Above the buildings of the Krummel factory there are 24,000 metres of metal wire with five million points, which may contribute in some measure to discharge the clouds, and would certainly conduct the lightning to earth after a discharge The ideal method would consist in using copper wire 1 cm. in diameter, but the expense of this would be enormous. The earth-contact is made in wet places with iron plates or rails one or two metres under the soil. Also the metal piping (if not replaceable by rubber tubing) and apparatus of the various parts of the factory are connected with the earth-conductors of the lightning conductors, so as to avoid the formation of sparks in the discharge of the lightning.

It has also been suggested that, where possible, the large vessels in the separate buildings should be electrically insulated, both from the lightning conductors and from the earth

[1] For *dynamites with active bases* (containing nitroglycerine, collodion-cotton or guncotton, nitrates, sawdust, &c), Stillman and Austin (1906) propose a method of analysis which is briefly as follows: The moisture is determined on 10 grms. as above; the dry mass is then extracted several times in the cold with a mixture of 1 part of alcohol and 2 parts of ether. The residue (*A*) is dried and weighed (for its analysis *see later*), the solution being left to evaporate in the cold to 100 c c., to which are added 100 c.c. of chloroform to precipitate the collodion-cotton. The liquid is decanted on to a tared, dry, cloth filter on to which all the *collodion-cotton* is brought by means of chloroform; the filter is dried in an oven at 40° and then in a desiccator and weighed (as a check, it is redissolved in alcohol and ether, reprecipitated with chloroform, collected on a filter and dried at 40°, the collodion being then detached from the filter, completely dried on a watch-glass in a desiccator and weighed). After the collodion-cotton is separated, the decanted and filtered liquids are evaporated in a tared vessel, dried in a vacuum and the remaining *nitroglycerine* weighed.

If the nitroglycerine contains traces of *nitrates*, these are extracted by repeated treatment with small quantities of water, the solution being then evaporated and the nitrates weighed. If along with the nitroglycerine there are also resin, paraffin, and traces of sulphur, it is titrated with excess of normal alcoholic caustic soda in the hot, the excess of alkali being then determined with normal acid in presence of phenolphthalein: 1 c.c. of normal alkali used in the saponification corresponds with 0·0757 grm. of *nitroglycerine* (in case no resin is present). After the titration, the liquid is evaporated almost to dryness to eliminate the alcohol and is then diluted with water and shaken with ether in a separating funnel.

The ethereal solution is separated and evaporated, and the residual paraffin weighed. The aqueous liquid

The resistance to heat of nitroglycerine and of dynamite is determined as with nitrocellulose (*see below*), the nitroglycerine being extracted from dynamite by displacement with water, and the gelatine explosives being mixed with double their weight of chalk prior to extraction with solvents; it should withstand a temperature of 70° for at least 15 minutes without colouring starch and potassium iodide paper. In contact with sensitive blue litmus paper it should not give the slightest reddening, as this would indicate incipient decomposition.

Exudation of nitroglycerine from dynamite, in either the cold or the hot, shows faulty manufacture.

With *nitrocellulose*, besides testing its solubility in a mixture of 1 part of alcohol and 2 parts of ether which dissolves collodion-cotton but not guncotton, the nitrogen is often estimated in the Lunge nitrometer (vol. i, p. 460) by shaking with concentrated sulphuric acid; or Schlosing's method, as used in France, may be employed to ascertain the type of the nitrocellulose: into a 150 c.c. flask are placed 25 grms. of pure, powdered ferrous sulphate, 0·7 to 0·8 grm. of nitrocellulose, and 70 to 80 c.c. of hydrochloric acid; the flask is shaken and then fitted with a stopper through which pass a delivery-tube and another tube conveying a current of carbon dioxide; when all the air is expelled the delivery-tube, dipping into a vessel of mercury, is covered with a graduated tube filled half with mercury and half with caustic soda solution. The flask is then heated to boiling, when the liquid blackens and in ten minutes all the nitric oxide is evolved, the last traces of this gas being driven out by a stream of carbon dioxide. The volume of gas gives the amount of nitrogen.

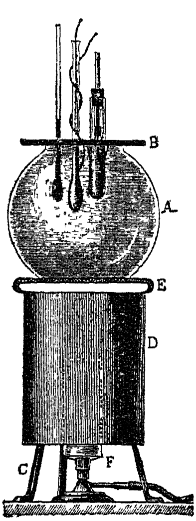


FIG. 223.

The amount of non-nitrated cotton is determined by boiling 5 grms. of the substance with a saturated solution of sodium sulphide, the liquid being decanted after a stand of 24 hours and the treatment with sodium sulphide repeated; the residue is finally collected on a tared cloth filter, washed with boiling water, then with dilute hydrochloric acid and lastly with boiling water again; it is then dried and weighed.

The *resistance to heat* (*Abel's heat test*) of nitrocellulose is of importance, as it serves as a control during manufacture and is used also as a test for nitroglycerine: a wide-mouthed glass flask, *A* (Fig. 223), 20 cm. in diameter, and with no neck, is almost filled with water and is covered with a leather disc pierced by four holes provided with wire clips for holding test-tubes; the flask is heated below by a small lamp, *F*, placed under a metal gauze and surrounded by a screen, *D*. The central aperture carries a thermometer, and one of the others a thermo-regulator (if necessary), whilst in the remaining ones are placed test-tubes which contain the nitrocellulose (1 to 3 grms.) or nitroglycerine (2 c.c.) and dip into the water. Each of the stoppers of the test-tubes is fitted with a hook of glass tubing on which is hung a piece of starch-potassium-iodide paper moistened at the upper part with a drop of dilute glycerine.

The temperature of the bath is maintained at 64° to 65° or at 80° to 82°, according to the commercial requirements of the explosive. The test is finished when a faint brown coloration appears at the edge of the glycerine. A good guncotton will withstand heating at 80° for half an hour without browning the paper.

after separation of the ethereal solution, is heated with a little bromine to oxidise the sulphur; it is then acidified with HCl, boiled, and the *resin* collected on a tared filter, whilst in the filtrate the sulphuric acid formed by oxidation of the *sulphur* is precipitated with $BaCl_2$.

The nitroglycerine may be estimated by difference, by subtracting from the original weight the insoluble residue, *A*, the paraffin, the resin, the small amount of sulphur, and the nitrates.

The residue, *A*, insoluble in alcohol and ether (*see above*), is extracted with hot water; the undissolved part is dried at 70° and weighed (*B* = sawdust + sulphur + any insoluble mineral substances); the *sulphur* is extracted with carbon disulphide, and weighed, this weight subtracted from *B* giving the *sawdust*, from which also the weight of ash left after calcining is subtracted if inorganic substances are present.

The aqueous solution obtained from *A* is evaporated, dried at 110° and weighed (*C* = nitrates + carbonates + any woody extract), it is then treated with a little nitric acid, evaporated, dried and weighed (*D*); from the difference between *C* and *D* the CO_2 evolved and hence the carbonates can be calculated.

The mass, *D*, is melted, heated to redness, cooled, treated with a little dilute nitric acid, evaporated, dried at 110° and weighed (*E*); this weight gives the sodium and potassium nitrates. Subtraction of the weights of nitrates (*E*) and carbonates from *C* gives that of the extractive matters and of ammonium nitrate, if this is present; this latter may be determined in the aqueous liquid, *A*, by estimating the ammonia evolved in the ordinary way.

Measurement of the Pressure or Heat of the Gases Developed by Explosives. The power of an explosive is deduced principally from the quantity of heat produced on explosion (*see* p. 216), this being measured in the Berthelot-Mahler calorimetric bomb (*see* vol. i, p. 372). Deflagration is induced by means of an electric spark, and if considerable pressure is maintained in the bomb by means of air (or nitrogen in the case of guncotton, as this is deficient in oxygen, which need not be supplied in order to reproduce the conditions of an ordinary explosion), the products of deflagration are almost identical with those of explosion. The bomb is specially constructed with various accessories to allow of the analysis and measurement of the gases produced in the decomposition, at either low or high pressure, of the explosive.

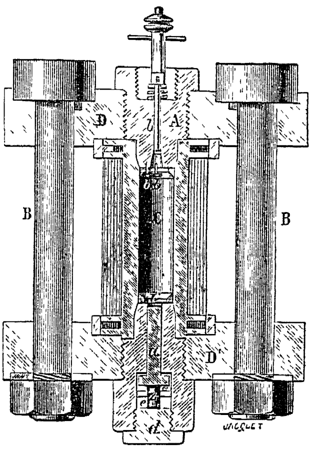


FIG. 224.

The *pressure* of the gases produced by the explosion in a resistant chamber, C (Fig. 224), of soft sheet steel wrapped round with steel wire, is measured indirectly by determining the crushing of a small copper cylinder, Z (*crusher*), 13 mm. high and 8 mm. in diameter, placed between a fixed base, d, and a hardened steel piston, a, of known surface which transmits the pressure of the gases. The chamber, C, is fixed by two massive wrought-iron plates, D and D', held together by six thick rods, B.

Deflagration is caused by rendering incandescent a platinum wire between the two terminals, b. In order to obtain exact results it is indispensable that there can be no escape of the gas, which would also cause danger from projection, the gas being at a temperature of 2000° to 3000° and a pressure of several thousand atmospheres.

The deformation of the *crushers* is shown in almost the natural dimensions in Fig. 179 on p. 219.

The *sensitiveness* of explosives to a *blow* is determined empirically by allowing a given weight of iron (*ram*) to fall from various heights on to a certain amount of explosive placed on an iron block, the height of the fall being increased until explosion occurs. The sensitiveness to *heat* is measured roughly by throwing small pieces of the explosive on to mercury heated to successively increasing temperatures until deflagration takes place.

When the *power of an explosive* cannot be determined directly or by comparison of the practical effects, indirect tests must be employed, although these do not always correspond with the actual effects. To avoid uncertainty, the expression *power of an explosive*, f, is applied to the product of the volume, v°, of gas (reduced to 0° and formed from unit weight of the explosive), the pressure, p_o, of 760 mm., and the absolute temperature, T (calculated from the products of the reaction), this product being divided by 273, so that:

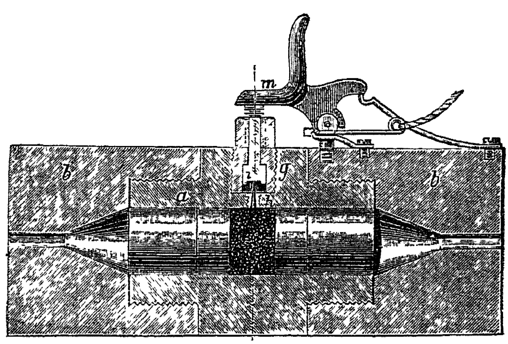


FIG. 225.

$$f = \frac{v_o p_o T}{273}.$$

The power of progressive explosives may be indirectly determined by Guttmann's power gauge (Fig. 225): on a hollow block of steel, a (diameter of cavity 35 mm.), are screwed two steel blocks, b, and a small firing-plug, g. A trigger, m, which can be released from a distance by means of a cord, serves to explode the plug. The apparatus is charged by unscrewing one of the blocks, b, and introducing first a cylinder of drawn lead, 40 mm. long and 35 mm. in diameter, which closes hermetically the wide mouth of the right-hand cone: then a steel disc and one of cardboard of such thickness that it makes 20 grms.

of powder rest just in the middle. This powder, which is introduced next, is situate just under the cap, *h*. Then follow a disc of cardboard, one of steel, and a block of lead similar to the first, this closing the cavity to the left, when the block, *b*, is again screwed on. The gases produced by the explosion have no outlet and so force the leaden blocks to the right and left into the conical holes to the right and left. The height of the leaden *cones* projecting is compared with that obtained with a standard explosive and thus gives the power of the explosive.

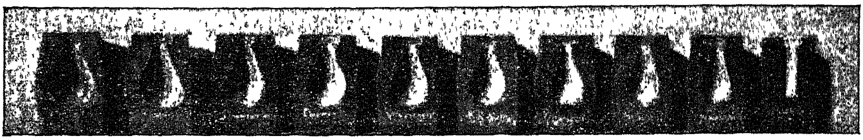


FIG. 226.

For shattering explosives, on the other hand, good results are obtained with Trauzl's *lead block*, which is in the form of a cylinder 200 mm. in height and diameter. In the middle is a cavity, 110 mm. deep and 20 mm. wide, into which 15 to 20 grms. of the explosive are placed. A fulminate cap, connected with wires for firing, is inserted and the bore tamped with well-compressed sand and chalk. After the explosion, the capacity of the cavity is measured with water. Fig. 226 shows several of these blocks after testing with various explosives. A charge of 15 grms. of No. 1 dynamite gives a volume of 705 c.c., and

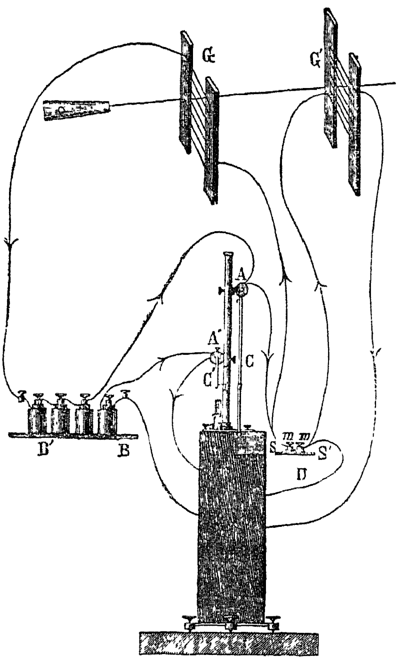


FIG. 227.

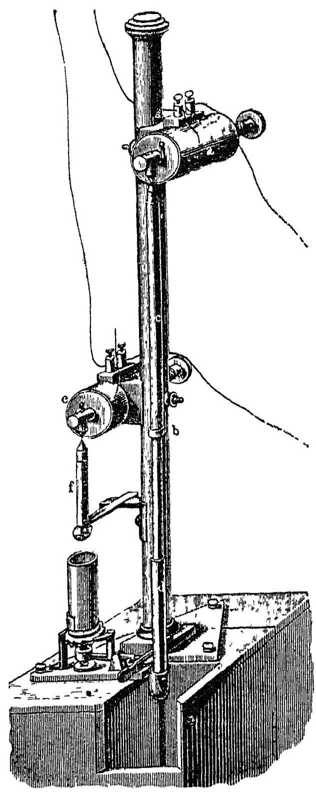


FIG. 228.

deducting from this 30 c.c. for the original volume, and 30 c.c. produced by the 1·5 grm. of fulminate in the cap, there remain 645 c.c. due to the explosive, *i.e.* 43 c.c. per gramme. To obtain comparable results with explosives of the same class, charges of equal weights must be taken, otherwise different values are obtained for the same explosive ; there are, besides, other causes of error, which give only a relative value to this method of determining the power.

Measurement of the Initial Velocity of Projectiles. For this purpose use is made of Le Boulengé's *chronograph* (Figs. 227 and 228), which gives the velocity, V, by measuring

the time, T, taken by the projectile to traverse the known distance, D (20 to 50 metres), between two wire frames, G, G' (Fig. 227), which are cut through by the projectile immediately after it leaves the gun and are connected electrically with two quite distinct points of the chronograph, the apparatus being so arranged that T lies between 0·05 and 0·15 second; $V = \frac{D}{T}$. The chronograph is formed of two electro-magnets, a and e (Fig. 218, or C and C', Fig. 217), joined to the batteries B and B', and to the corresponding wire frames, G and G'. The magnet, a, attracts a tubular bar (c, d, Fig. 228, or C, Fig. 227) of the *chronometer*, which terminates at the top in a soft iron point and is enlarged at the bottom; the magnet, e (or A' in Fig. 227), attracts a rod, f (or C', Fig. 227), of the *registrar*. The chronometer bar is surrounded by a thin zinc or copper tube. The registrar is of soft iron, has the same weight as the chronometer, and is pointed at the top and enlarged at the bottom. When the projectile traverses the first frame, G, it interrupts the current of the electro-magnet, A, and the chronometer bar, C, becomes detached from A (Fig. 227) and begins to fall freely. When it traverses the second frame, G', it interrupts the current of the electro-magnet, A', and the registrar, C', falls and releases a hook which liberates a horizontal spring pointer, this immediately striking the falling chronometer bar. The mark on this bar will be the higher the lower the initial velocity of the projectile. Suitable tables deduced from simple formulæ [1] give the required velocity.

The velocity of detonation is difficult to determine, since it depends largely on the resistance of the enclosure containing the explosive and on other circumstances. It is determined roughly but with sufficient exactitude, under similar conditions, by placing a number of cartridges in a continuous row and joining the two wires of the Le Boulengé chronograph to points in the row at a certain distance apart.

USES OF EXPLOSIVES. The largest consumption of explosives is that of armies and navies, whilst in various civil operations these substances are also employed: in the tunnelling of mountain ranges separating various races; in lessening manual labour in the ploughing of the soil; for disintegrating rocks to provide material for the construction of houses to displace the all too numerous deserts; and further, for preparing blocks of material to be wrought by the genius of man into monuments attesting to posterity the varied and incessant progress of human thought and labour.

In practice a sharp distinction is made between progressive explosives, used more especially in mines for detaching large masses of rock and for excavating (for coal, minerals, gold, and diamonds), and shattering explosives (dynamite, &c.), employed for such purposes as demolishing walls, bridges, and large trees, or breaking the ice at the surface of rivers and lakes when navigation is prevented. To demolish a large tree it is sufficient to surround it with a string of dynamite cartridges, explosion of one of which will cause explosion of the others; to break iron, *e.g.* a railway rail, or cut a bridge, one or more cartridges are placed on it, covered with a light tamping of earth and exploded. In subaqueous works modern smokeless explosives are of great service, since to their great power is added their stability towards water, which acts as an excellent tamping.

STATISTICS OF EXPLOSIVES. In 1908 Italy produced 764 quintals of cheddite, 580 of solenite, 556 of prometheus, 280 of guncotton, 2153 of collodion-cotton, 56 of

[1] A test is first made in which the chronometer bar and the registrar fall simultaneously The height, h, at which the former is struck corresponds with a time, t, which must always be allowed for in the subsequent measurements, as it represents the time required by the registrar to release the spring. According to the law of bodies falling freely, $h = \frac{1}{2}gt^2$, so that $t = \sqrt{\frac{2h}{g}}$; in practice, when a time, T, elapses during the passage of the projectile from G to G', the mark on the chronometer bar at the height, H, corresponds with a time, $T + t = \sqrt{\frac{2H}{g}}$. The difference between these two measurements gives the time required, the velocity being then deduced from the formula: $V = \frac{D}{\sqrt{\frac{2}{g}}\left(\sqrt{H} - \sqrt{h}\right)}$.

fulminate of mercury, and 23,000 of powder for fireworks. The various explosives factories in Italy employ almost 3000 workmen.

The consumption of explosives in time of war is enormous. Every shot of a large gun, which does not always hit the mark, costs hundreds of pounds. In the last Russo-Japanese war, the besiegers of Port Arthur blew up part of one of the forts with a mine containing 5000 kilos of dynamite. During the piercing of the Simplon, 1640 tons of gelatine explosives were used, mostly with a content of about 92 per cent. of nitroglycerine. In constructing the harbour of Genoa, the Nobel Company exploded simultaneously a number of mines with a total charge of 6000 kilos of dynamite. For the removal in 1905 of a rock that partially obstructed the Danube at Greisenstein, a mine was laid with 11,700 kilos of dynamite; 280,000 cu. metres of rock were detached at a cost of about three-halfpence per cubic metre. In the American Independence Day fêtes, a million pounds worth of fireworks are consumed every year.

In addition to its enormous home consumption, Germany exported, in 1906, 2136 tons of black powder of the value of £320,000; 4791 tons of other explosives, worth £372,000; and 7300 tons of cartridge charges for guns and artillery, of the value of £1,000,000.

In the United States the industry is a rapidly growing one. While the total production was £3,400,000 (including 40,000 quintals of dynamite) in 1900, it rose in 1905 to £5,920,000, of which £1,760,000 represented black powder; £320,000 nitroglycerine; £3,200,000 dynamite; £800,000 smokeless powder; and £35,200 guncotton.

In 1909 the United States possessed 86 explosives factories with a total capital of £10,000,000 and a total annual output of the value of £8,000,000.

The *world's production* of explosives reaches a total of 350,000 to 400,000 tons, almost the half of this amount being made in the United States. According to O. Guttmann, the production of explosives with nitroglycerine as base amounted in 1909 to more than 62,000 tons, distributed as follows: United States, 20,000 tons; Germany, 10,300; England, 8100; the Transvaal, 8000; Canada, 5000; Spain and Portugal, 3500; Austria-Hungary, 2300; France, 1500; Switzerland, Australia, and Norway and Sweden, 600 each; Russia, Italy, and Holland and Belgium, about 500 each; and Greece, 175 tons. For dynamite for military purposes, Japan requires annually 9000 quintals of nitroglycerine, and consumes, in addition, 9000 quintals of other powders. Only a small portion of these is manufactured in Japan, which imports every year explosives of the value of £80,000 (from England, Germany, and Belgium); in 1909 the Armstrong firm erected a cordite factory near Yokohama. In the Transvaal mines explosives to the value of £1,440,000 were consumed in 1910.

EE. ACIDS

I. SATURATED MONOBASIC FATTY ACIDS, $C_nH_{2n}O_2$

These are termed *fatty* acids because some of them are contained in fats, from which they are prepared. All contain the characteristic group, $-CO_2H$, the hydrogen of which is replaceable by metals. With every hydrocarbon or every primary alcohol of the methane series corresponds a monobasic fatty acid. The first members are liquids having a pungent odour, and are soluble in water, alcohol, or ether, and boil without decomposing; then follow members of an oily consistency, less soluble in water, and with unpleasant smells like that of rancid butter or perspiration; beyond C_{10} they are solid, insoluble in water, soluble in alcohol or ether, and distilling unchanged only in a vacuum. The first members (up to C_9 or C_{10}) are volatile in steam.

It will be seen that the boiling-points of these acids rise regularly with increase in the number of carbon atoms, but the melting-points are higher in an acid with an even number of carbon atoms than in those immediately below and above with uneven numbers.

GENERAL METHODS OF PREPARATION. (*a*) In dealing with primary alcohols and aldehydes, it was shown how simple oxidation of these compounds yields the corresponding acids containing the same number of carbon atoms, whilst when secondary and tertiary alcohols or ketones are

TABLE OF THE SATURATED MONOBASIC FATTY ACIDS

Formula	Name	Melting-point	Boiling-point	Specific gravity
CH_2O_2	Formic	+ 8·3°	101°	1·2187 (20°)
$C_2H_4O_2$	Acetic	+ 16·5°	118°	1·0502 (20°)
$C_3H_6O_2$	Propionic	– 22°	141°	1·013 (0°)
$C_4H_8O_2$	Normal butyric	– 7·9°	162°	0·987 (0°)
	Isobutyric	– 79°	154°	0·965 (0°)
$C_5H_{10}O_2$	Normal valeric	– 58·5°	185°	0·956 (0°)
	Isovaleric	– 51°	174°	0·947 (0°)
	Trimethylacetic	+ 34°–35°	163°	0·905 (50°)
	Methylethylacetic	—	173°–174°	0·938 (20°)
$C_6H_{12}O_2$	Normal caproic (hexoic)	– 1·5°	205°	0 945 (0°)
$C_7H_{14}O_2$	Normal heptoic	– 10°	223°	0·921 (15°)
$C_8H_{16}O_2$	Caprylic (octoic)	+ 16·5°	237·5°	0·910 (20°)
$C_9H_{18}O_2$	Pelargonic (nonoic)	+ 12·5°	186° At 100 mm. pressure.	0·911 (12°)
$C_{10}H_{20}O_2$	Capric (decoic)	+ 31·4°	200°	0·930 (37°)
$C_{11}H_{22}O_2$	Undecoic	28°	212°	—
$C_{12}H_{24}O_2$	Lauric	44°	225°	0·875 At melting-point.
$C_{13}H_{26}O_2$	Tridecoic	40·5°	236°	—
$C_{14}H_{28}O_2$	Myristic	54°	248°	0·862
$C_{15}H_{30}O_2$	Pentadecoic	51°	257°	—
$C_{16}H_{32}O_2$	Palmitic	62·6°	268°	0·853
$C_{17}H_{34}O_2$	Margaric	60°	277°	—
$C_{18}H_{36}O_2$	Stearic	69·3°	287°	0·845
$C_{19}H_{38}O_2$	Nonadecoic	66 5°	298°	—
$C_{20}H_{40}O_2$	Arachidic	77°	—	—
$C_{22}H_{44}O_2$	Behenic	84°	360°/60 mm.	—
$C_{24}H_{48}O_2$	Lignoceric	80°–81°	—	—
$C_{26}H_{52}O_2$	Cerotic	78·5°	—	—
$C_{30}H_{60}O_2$	Melissic	91°	—	—

oxidised, the chain is broken and acids with a less number of carbon atoms are obtained.

(*b*) Hydrolysis of the *nitriles* (*see these*) in the hot with potassium hydroxide or with mineral acids yields the amides (*see these*) as intermediate compounds, and then the acids with one carbon atom more than the alcohols from which the nitriles originate :

$$CH_3\cdot CN + 2H_2O = NH_3 + CH_3\cdot CO_2H.$$

(*c*) The interaction of a zinc-alkyl with phosgene gives :

$$Zn(CH_3)_2 + 2COCl_2 = ZnCl_2 + 2CH_3\cdot COCl \text{ (Acetyl chloride)},$$

which, on decomposition with water gives :

$$CH_3\cdot COCl + H_2O = HCl + CH_3\cdot CO_2H.$$

(*d*) When a hydroxy-acid is heated with hydrogen iodide, separation of water and iodine occurs and a fatty acid is formed.

(*e*) Other general reactions are those of Grignard (*see* p. 203), those of ethyl acetoacetate and ethyl malonate (*see these*), and those of elimination of CO_2 from dibasic acids (containing two carboxyls, $CO\cdot OH$) and of addition of hydrogen to unsaturated acids, &c.

PROPERTIES. In aqueous solution the acids are electrolytically dissociated into the *cations* H and the *anions* $R\cdot CO_2$ (*see* vol. i, p. 91).

Substitution of this ionic hydrogen by a metal yields *salts*, which in aqueous solution (when they are soluble) are almost completely dissociated, whilst the

hydrogen of the alcohols is also replaceable by a metal (alkoxide), but the resulting alkoxide is decomposed by water (hydrolysed).

The strength of an acid (or its power) can always be determined from the degree of dissociation (vol. i, p. 98) this decreasing in the following order: formic, acetic, propionic, normal butyric, valeric, &c.; thus, with rise of the molecular weight the dissociation diminishes.

The hydroxyl group of the carboxyl group, $-CO \cdot OH$, can sometimes be substituted by halogens (especially by chlorine, by the action of PCl_5, which forms acid chlorides or *chloroanhydrides, e.g.* acetyl chloride, $CH_3 \cdot COCl$).

Substitution of the hydroxyl, (1) by SH, gives *thio-acids*, and (2) by NH_2 yields the *amides, e.g.* acetamide, $CH_3 \cdot CO \cdot NH_2$ (by heating ammonium acetate); under certain conditions these compounds all give the acids from which they originate.

It has already been mentioned that the saturated hydrocarbons are formed by the electrolysis of the alkali salts of the corresponding acids, with elimination of CO_2, H, and O (the last two from the water present as solvent) and also of secondary products (unsaturated ethers and hydrocarbons); if the electrolysis is effected without a diaphragm, alkaline carbonate and bicarbonate are formed, and hence also a lower alcohol. Carbon dioxide can also be eliminated, and hydrocarbons thus formed, from the alkali salts of the acids by heating in presence of soda-lime or baryta, or by reducing the acids with hydriodic acid and phosphorus.

But if the calcium salts of the acids are distilled, with or without P_2O_5, the principal product is a ketone formed from two molecules of the acid:

$$(CH_3 \cdot COO)_2Ca = CaCO_3 + CH_3 \cdot CO \cdot CH_3\,;$$

if the calcium salt is heated in presence of calcium formate, the aldehyde corresponding with the higher acid is formed.

The halogens also replace the hydrogen of the alkyl residues of the acids, giving products which surpass in acids properties the acid from which they are formed.[1] By heating the acids homologous to acetic acid (which are very

[1] Besides referring to what has been stated in vol i, p. 91 *et seq*, we may here quote the very clear consideration of this question given by Professor Miolati on the **Affinity Constants of Acids.** That different acids possess different strengths follows, for example, from the phenomenon of displacement of one acid from its salts by another acid. When sulphuric acid is added to a solution of sodium acetate, the characteristic odour of acetic acid is perceived, since the sulphuric acid is transformed into sodium sulphate and a certain amount of acetic acid is liberated. This quantity and, in general, the quantity of any acid displaced by a second acid, is not equivalent to the amount of the latter added, but the two acids divide the base according to their strengths, *i.e.* according to their affinity constants, and also to their quantities. The effect of the latter factor may be eliminated by using equivalent quantities of the two acids and of the base, *e.g.* by causing an equivalent of an acid to act on an equivalent of neutral salt, so that the distribution of the base between the two acids depends only on their strengths. A chemical equilibrium is then established which is represented by the equation.

$$(1 - x)[NaX + HX'] \rightleftarrows x[NaX' + HX].$$

In order that this method may give exact results, it is of course necessary that the bodies formed in the conditions of the experiment be not eliminated either as gas, or solid, or complex molecules, &c., but that they remain to take part in the equilibrium. To determine this, Thomsen made use of the thermal change and Ostwald the changes of volume and the indices of refraction, these methods leading to the same results In general, any physical property may be used for the analysis of the equilibrated system.

If, for example, a is the heat-change observed on neutralising an equivalent of the first acid with a base, b the corresponding quantity for the second acid, and c that observed on adding an equivalent of base to an equivalent of the mixed acids, it is evident that c will be equal to the thermal effect of the neutralisation of a certain fraction of an equivalent of the first acid $(1 - x)$ plus the thermal effect of the neutralisation of the complementary fraction of the second acid:

$$c = (1 - x)a + x\,b\,; \quad x = \frac{a - c}{a - b}; \quad (1 - x) = \frac{c - b}{a - b}.$$

$\frac{x}{(1 - x)}$ is a measure of the relative affinities of the two acids. The following Table gives certain values of x determined by Ostwald, x indicating the fraction of the molecule of base taken up by the acid given first:

		x			x
$HNO_3 : CHCl_2 \cdot COOH$	..	0 76	$H \cdot COOH : CH_3\ COOH$	..	0·76
$HCl . CHCl_2 \cdot COOH$	..	0·74	$H \cdot COOH : C_2H_5\ COOH$	..	0·79
$CCl_3 \cdot COOH : CHCl_2\ COOH$	..	0 71	$H \cdot COOH : C_3H_7 \cdot COOH$ norm.	..	0·80
$CCl_3 \cdot COOH : CH_2Cl \cdot COOH$	..	0·92	$H \cdot COOH : C_3H_7 \cdot COOH$ iso	..	0 81
$CCl_3 \cdot COOH ; H \cdot COOH$	..	0·97	$CH_3 \cdot COOH ; C_3H_7 \cdot COOH$ (norm)	..	0 53

resistant to oxidising agents) with concentrated sulphuric acid, CO_2 is evolved, whilst acids with carboxyl united to a tertiary carbon atom (*e.g.* formic or trimethylacetic acid) evolve CO and are transformed by oxidising agents into hydroxy-acids: $(CH_3)_2:CH\cdot COOH$ gives $(CH_3)_2:C(OH)\cdot COOH$.

Separation of the fatty acids from mixtures of them is not always easy and is sometimes effected by taking advantage of their greater or less volatility either in steam or in a vacuum, or by precipitating with magnesium acetate or barium chloride, since in alcoholic solution the higher acids are precipitated first. Use is also made of the fractional solution of the calcium, barium, or lead salts in various solvents (alcohol, ether, &c.), or of fractional neutralisation followed by distillation of the acids not neutralised. From an aqueous mixture of formic, acetic, butyric, and valeric acids, the last two can be separated by extraction with benzene, from which they can be isolated by shaking with baryta water. Further separation can then be effected as above.

If we calculate $\frac{x}{1-x}$, making nitric acid equal to 100, we obtain the following values:

Nitric acid	100	Formic acid	3 9
Hydrochloric acid	98	Propionic acid	1 04
Trichloroacetic acid	80	Butyric acid	0 98
Dichloroacetic acid	33	Glycollic acid	5 0
Monochloroacetic acid	7	Lactic acid	3 3
Acetic acid	1 23		

The acids arrange themselves in the same order and almost with the same coefficients, if other properties are studied. All acids possess, for example, the property of accelerating certain hydrolyses, such as that of ethyl acetate and the inversion of cane sugar:

$$CH_3\cdot COOC_2H_5 + H_2O = C_2H_5\cdot OH + CH_3\cdot COOH;$$
$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6.$$

In these reactions the acid added acts only by its presence (catalysis), since at the end of the reaction it remains unchanged. But, on the addition of equivalent quantities of various acids, the reactions take place with greater or less velocities, *i.e.* the same quantity of ethyl acetate or cane-sugar is transformed in a longer or shorter time according to the acid added. The velocity of the reaction is proportional to the affinity constant of the acid. Finally, the acids are arranged in the same order if we compare their electrical conductivities. According to the theory of electrolytic dissociation, the value of the conductivity depends on the number of molecules of the dissolved acid which are dissociated into their ions, *i.e.* into hydrogen ions on the one hand, and acid ions on the other. *The possibility of furnishing hydrogen ions in aqueous solution would hence be characteristic of the acid nature of a substance, the amount of these hydrogen ions in unit volume being a measure of the acidity.* With equivalent solutions of different acids, the strong acids will be those which contain, in a given volume of the solution, a large number of hydrogen ions, and the weak ones those containing only a small number of such ions.

The condition of an acid in solution may hence be represented by the expression:

$$AH \rightleftarrows A' + H^{\cdot}$$

and we may term the fraction of the equivalent which is dissociated, the *degree of dissociation*, α. Without entering into further details it may be mentioned that α is related, besides, to the electrical conductivity, also to van 't Hoff's coefficient i, which expresses the divergence of the osmotic behaviour of solutions of electrolytes from the normal behaviour (*see* vol. i, p 99).

The degree of dissociation varies with the concentration of the solution of the acid, increasing with the dilution towards the limiting value 1, which corresponds with complete dissociation. This increase is small for strong acids, *i.e.* those which contain a considerable number of hydrogen ions even in concentrated solutions, but is much greater for the weak acids.

	v	$100\,\alpha$	
$CH_3\cdot COOH$	32	2 38	1
	1024	12 66	4·22
CH_2Cl COOH	32	19 9	1
	1024	68·7	3 53
$CHCl_2$ COOH	32	70 2	1
	1024	99·7	1 42

v indicates the number of litres of solution containing 1 grm.-mol. of the acid.

The affinity constants given above hence depend on the concentration of the acid, since with this the concentration of the hydrogen ions—on which the value of the acid properties of a substance depends—varies. An expression which is independent of v can, however, be found by considering the equilibrium: $HA \rightleftarrows H^{\cdot} + A'$, as if it were a gaseous equilibrium and applying the law of mass action to it. If α is the fraction of the equivalent which is dissociated, $(1-\alpha)$ will be that of the non-dissociated part; and, if v is the number of litres in which the gramme-equivalent is dissolved, $\frac{\alpha}{v}$ will be the so-called active mass of the ions, *i.e.* the number of ions contained in unit volume, and $\frac{1-\alpha}{v}$ the number of undissociated molecules in the same unit volume. The law of mass action gives:

$$\left(\frac{1-\alpha}{v}\right)k = \left(\frac{\alpha}{v}\right)\left(\frac{\alpha}{v}\right);\quad k = \frac{\alpha^2}{(1-\alpha)v}$$

where k is a constant depending solely on the nature of the equilibrium—that is, on the nature of the reacting

Constitution of the Fatty Acids. That these acids actually contain carboxy groups, —COOH, is indicated by the different ways in which they are formed and decomposed, but the most characteristic method of preparation consists of the hydrolysis of the nitriles, which are obtained from the alkyl iodides by the action of potassium cyanide (*see* p. 198). Two molecules of water react with one of nitrile, giving ammonia and a higher acid :

$$CH_3\cdot C : N + 2H_2O = NH_3 + CH_3\cdot COOH.$$

The nitrogen of the nitrile being detached, the group —COOH must necessarily be formed, since, from reasons already mentioned, the formation of a group $-C(OH)_3$ is excluded, as three free hydroxyl groups cannot remain united to one carbon atom (although the corresponding *ortho-ethers* are known and also acetals, *see* pp. 182, 205, and 209).

FORMIC ACID, $H-C\begin{array}{l}\nearrow O\\ \searrow OH\end{array}$

Methanoic Acid

It was shown as early as the seventeenth century that ants contained a special acid, which was characterised later as formic acid, and was separated (by distilling with water) from the wood ant, the migratory ant, bees (and hence from crude honey), the hairs of the nettle, pine leaves, perspiration, urine, &c.

Until recently, in spite of numerous processes by which it can be synthesised (*e.g.* by hydrolysing, with acid or alkali, hydrocyanic acid, which

bodies—and on the temperature ; k is hence a measure of the tendency of an acid to dissociate and is called the *affinity constant*

The following Table gives the numbers referring to acetic acid and two of its chloro-derivatives :

v	Acetic acid			Monochloroacetic acid			Dichloroacetic acid		
	Δ	$100\ \alpha$	$10^5 k$	Δ	$100\ \alpha$	$10^5 k$	Δ	$100\ \alpha$	$10^5 k$
16	6 5	1·67	1 79	56 6	14 6	155	—	—	—
32	9 2	2 38	1 82	77 2	19·9	155	269 8	70 2	5170
64	12 9	3 33	1 79	103·2	26 7	152	309 9	80 5	5200
128	18·1	4 68	1 79	136 1	35 2	150	338 4	88 0	5040
256	25 4	6 56	1 80	174 8	45 2	146	359 2	93 4	5160
512	34 3	9 14	1 80	219 4	56 8	146	375 4	97·6	—
1024	49 0	12·66	1·77	265 7	68 7	147	383 8	99 7	—

In this Table Δ denotes the molecular conductivity corresponding with the dilution v, 100 α the extent of dissociation in per cent., and $10^5 k$ the affinity constant multiplied by 100,000

This affinity constant has a markedly constitutive character; it increases, for instance, if a substituent of negative nature, such as OH, Cl, N, NO_2, &c., enters a molecule and decreases if positive groups such as NH_2 enter. The following examples may be given :

Formic acid	$k = 127\ 0.10^{-5}$
Acetic acid	$1\ 8.10^{-5}$
Propionic acid	$1{\cdot}3.10^{-5}$
Substitution with halogens and similar groups.	
Monochloroacetic acid	$k = 155.10^{-5}$
Dichloroacetic ,,	$= 5100\ 10^{-5}$
Trichloroacetic ,,	about $120{,}000.10^{-5}$
Bromoacetic ,,	138.10^{-5}
Cyanoacetic ,,	370.10^{-5}
Thiocyanoacetic ,,	260.10^{-5}
β-Iodopropionic ,,	$9\ 0.10^{-5}$
Substitution by hydroxyl.	
Glycollic acid, $OH\cdot CH_2\cdot COOH$	$k = 15{\cdot}0\ 10^{-5}$
Lactic acid, $CH_3\ CH(OH)\ COOH$	$14\ 0.10^{-5}$
β-Hydroxypropionic acid, $OH\cdot CH_2\ CH_2\cdot COOH$	$3{\cdot}1\ 10^{-5}$
Substitution by NH_2.	
α-Aminopropionic acid (alanine), $CH_3\ CH(NH_2)\ COOH$	$k = 9\ 0.10^{-5}$

For further examples and greater details, *see* R. Abegg's "The Electrolytic Dissociation Theory," New York, 1907.

may be regarded as the nitrile of formic acid), it was prepared almost exclusively by heating crystallised oxalic acid with glycerine free from water in a reflux apparatus, the formic acid thus obtained being distilled. For some years, however, this acid has been prepared very cheaply by Goldschmidt's process (Ger. Pat. 86,419 and Fr. Pats. 342,168 and 362,417), which consists in first forming sodium formate by the action of carbon monoxide under pressure [or of generator gas (vol. i)] on powdered sodium hydroxide or, better, by dropping on to coke heated to 200° to 220° a solution of sodium hydroxide, carbonate, or sulphate and then passing in a hot current of carbon monoxide. Similarly from milk of lime and coke at 250°, calcium formate is obtained.

From the dry salts, almost anhydrous formic acid is then obtained by treatment with cold concentrated sulphuric acid to which formic acid, already in the free state, is initially added (Fr. Pats. 341,764 and 393,526); the pure acid was formerly obtained, but with considerable loss, by distilling its salts with concentrated sulphuric acid.

According to Eng. Pat. 8438 of 1910, better results are obtained by running 35 parts of concentrated sulphuric acid into 200 parts of concentrated formic acid, shaking meanwhile; to this mixture quantities of 50 parts of the dry formate and 50 parts of concentrated sulphuric acid are added alternately. Good results are also obtained by decomposing the formates by means of hydrofluoric acid (Ger. Pat. 209,418, 1907). *See also* U.S. Pats. 970,145 of 1910 (W. H. Walker) and 975,151 of 1910, in which the decomposition of formates by phosphoric acid below 145° is proposed.

This new process makes it advantageous to prepare oxalates from formates, whilst the latter were previously obtained from the oxalates. According to Fr. Pat. 413,947 of 1910, the formate is run into an evacuated vessel maintained at 550° to 600° by means of a metal bath; if the temperature of the mass introduced is kept for half an hour at above 400°, the formate is transformed quantitatively into pulverulent oxalate (150 kilos for every square metre of heated surface).

Almost anhydrous formic acid is obtained by distillation over anhydrous copper sulphate (Ger. Pat. 230,171, 1909).

Pure formic acid is a colourless liquid with a pungent odour, sp. gr. 1·223 at 0°, b.pt. 99°; it solidifies on cooling and then melts at 8·6°. If poured on the hand it produces very painful blisters. In aqueous solution, a mixture of constant composition distils, as is the case with hydrochloric acid (vol. i, p. 158); at ordinary pressure this mixture contains 77·5 per cent. of acid and boils at 107°. Unlike its homologues (acetic, butyric acid, &c.), it is readily oxidised by permanganate, &c., forming CO_2 and H_2O; hence its great *reducing power*, owing to which, in the hot, it separates silver from silver salts, and first mercurous chloride and then mercury from mercuric chloride solutions. Thus it behaves as an aldehyde, the characteristic group of which, $-C\begin{smallmatrix}\nearrow O \\ \searrow H\end{smallmatrix}$ it does indeed contain. When heated in a sealed tube at 160° or treated with concentrated sulphuric acid, it decomposes readily and completely into $CO + H_2O$. Finely divided rhodium, ruthenium, or iridium (but not platinum or palladium) decomposes it completely into CO_2 and H_2. Various bacteria produce the same change.

Its price has now fallen to below 72*s*. per quintal (85 per cent. concentration) and owing to its low molecular weight it can compete with acetic acid, a less weight being required to produce a given acidity. On account of its acid character and its reducing and antiseptic properties, it is used to increase the yield of alcoholic fermentations, in the dyeing and printing of textiles where it can replace lactic acid (not always advantageously), in the bichromate mordanting of wool, and also acetic acid (in France the consumption of acetic acid has diminished from this reason). Its use in tanning has also been suggested.

Its strength is determined by means of standard sodium hydroxide solutions, using

phenolphthalein as indicator, but when other acids are also present it is titrated with permanganate in acid solution or chromic acid in alkaline solution. The CO evolved when it is treated with concentrated sulphuric acid can also be measured. When other organic acids are present, the dilute mixture is treated with mercuric acetate at the boiling temperature, the mercurous acetate which separates being filtered off in the cold, dissolved in nitric acid, the calomel precipitated with sodium chloride then being weighed. Or dilute formic acid solution (0·2 grm. per litre) may be treated with about 15 times the weight of mercuric chloride (calculated on the acid) dissolved in 200 c.c. of hot water, the liquid being well shaken and the mercurous chloride precipitate, after treatment with caustic soda, collected on a Gooch crucible, washed, dried, and weighed; multiplication of the weight by 0·097726 gives the weight of formic acid (Franzen and Greve, 1909). Formic acid may be detected, even in presence of aldehydes, acetic acid, and methyl alcohol, by means of sodium bisulphite solution, which gives a reddish yellow coloration.

Presence of hydrochloric acid as impurity may be detected by dilution (1 : 20) and addition of silver nitrate: oxalic acid may be detected by saturating with ammonia and adding calcium chloride. If no acrolein or allyl alcohol is present, it does not give a pungent odour after neutralisation with caustic soda.

The commercial aqueous acid costs 24*s.* per quintal for a 25 per cent. solution (sp. gr. 1·064); 44*s.* for 50 per cent. solution (1·124); 62*s.* for 75 per cent. solution (1·170); 72*s.* for 85 per cent. (1·190); and 108*s.* for the 96 to 98 per cent. acid (1·217) The chemically pure acid costs more than double these prices.

SALTS OF FORMIC ACID are called *formates* and are generally soluble in water and crystallisable; almost all the characteristic properties and reactions of formic acid (reduction, &c.) are shown also by its salts. With concentrated sulphuric acid in the hot, they yield carbon monoxide. Formates are obtained by the action of carbon monoxide on metallic hydroxides in the hot and under pressure (*see* also Fr. Pat. 382,001, 1907, and U.S. Pat. 875,055, 1907). When heated at 200° to 400°, the formates yield carbonates and oxalates and chemically pure hydrogen *Potassium formate*, $H \cdot COOK$, forms deliquescent crystals. *Sodium formate*, $H \cdot COONa$, crystallises well with $3H_2O$ at 0° or with $2H_2O$ at 17° and melts at 253° (the pure salt costs 3*s.* 7*d.* per kilo, and the commercial salt, 1*s.* 7*d.*). *Ammonium formate*, $H \cdot COONH_4$, melts at 115° and at a higher temperature decomposes into formamide, water, and a little hydrocyanic acid; since, in its decomposition when heated, it gives nitrogen and carbon compounds, it is used to harden and cement steel (the pure salt costs as much as 9*s.* 6*d.* per kilo). The magnesium, barium, and calcium salts are also soluble in water; the last costs 4*s.* (pure) or 2*s.* (impure) per kilo. *Lead formate* $(H \cdot COO)_2Pb$, dissolves only slightly in cold water, but readily in hot, and hence serves well to separate formic from other acids. *Zinc formate*, $(H \cdot COO)_2Zn$, is insoluble in absolute alcohol and hence also serves to separate formic acid from others. *Acid formates*, such as $H \cdot COONa + H \cdot COOH$, are also known.

ACETIC ACID, $CH_3 \cdot C \begin{smallmatrix} \diagup O \\ \diagdown OH \end{smallmatrix}$

Ethanoic Acid

Although its constitution was first determined by Berzelius in 1814, acetic acid has been known from the earliest times, since it forms easily in wine (vinegar), in many vegetable juices, in sour milk, in perspiration, in excreta, &c. In 1700 Stahl obtained it in a concentrated form by freezing the dilute acetic acid, then neutralising with alkali and distilling the acetic acid after addition of sulphuric acid. It is often formed in the oxidation and combustion of many organic substances; of the various synthetic processes for its preparation, that of Kolbe (1843) may be mentioned: perchlorethane, in presence of water and under the influence of light, gives trichloroacetic acid: $CCl_3 \cdot CCl_3 + 2H_2O = 3HCl + CCl_3 \cdot COOH$, and this is reduced by nascent hydrogen to acetic acid. Commercially it is obtained from ethyl alcohol and, especially, by the dry distillation of wood (*see later*).

PROPERTIES. When pure, acetic acid forms a colourless liquid of sp. gr. 1·0553 at 15° and a specific heat of 0·522 between 26° and 96°, it solidifies at +16·7° in white crystals (hence the name *glacial acetic acid*, which is very hygroscopic and has the sp. gr. 1·08 at 0°) and boils at 118°, but evaporates considerably below this temperature owing to its high vapour pressure. It is soluble in all proportions in water, alcohol, and ether. Its vapours burn with a bluish flame. It dissolves many organic and several inorganic substances (P, S, HCl, &c.). When pure concentrated acetic acid is mixed with water, heating and contraction take place; the specific gravity increases on dilution of the pure acid and reaches a maximum (1·0748) with 77 per cent. of the acid (corresponding with the hydrate, $C_2H_4O_2 + H_2O$), afterwards diminishing gradually as the dilution increases.[1] Hence when the density of an acetic acid solution is given it must be indicated whether it refers to solutions containing more or less than 77 per cent. of the acid. It cannot, however, be assumed that a chemical compound, $C_2H_4O_2 + H_2O$, actually corresponds with the maximum density of the aqueous solution, since at other temperatures the maximum densities correspond with different compositions; thus, at 0° the maximum density is obtained with 80 per cent. of acetic acid and at 40° with 75 per cent. The *strength* of acetic acid generally refers to the weight and not to the volume of the acid.

The lowest freezing-point is obtained (−27°) with the aqueous solution containing 60 per cent. of the acid (corresponding with a hydrate, $C_2H_4O_2 + 2H_2O$), whilst solutions with 84 per cent. and with 10 per cent. freeze at −3·2°. Unlike those of formic acid and of mineral acids, aqueous solutions of acetic acid yield no distillate of constant composition.

The vapour density of the acid indicates a mixture of simple and double molecules below 250°, and simple molecules alone above this temperature. With hydrogen bromide it forms reddish crystalline additive products, *e.g.* $CH_3\cdot COOH, Br_2, 4HBr$. Certain bacteria decompose it into $CH_4 + CO_2$.

In contact with red-hot pumice, acetic acid vapour only partially decomposes, giving acetone, CO_2, and a little phenol and benzene. Chlorine replaces

[1] Oudeman's Table: specific gravity and concentration of acetic acid at 15°.

Specific gravity	Per cent. of acid by weight	Specific gravity	Per cent of acid by weight	Specific gravity	Per cent of acid by weight	Specific gravity	Per cent. of acid by weight	Specific gravity	Per cent. of acid by weight
1·0007	1	1·0185	13	1·0412	30	1·0646	54	1·0748	78
1·0014	1·5	1·0192	13·5	1·0424	31	1·0653	55	1·0748	79
1·0022	2	1·0200	14	1·0436	32	1·0660	56	1·0748	80
1·0030	2·5	1·0207	14·5	1·0447	33	1·0666	57	1·0747	81
1·0037	3	1·0214	15	1·0459	34	1·0673	58	1·0746	82
1·0045	3·5	1·0221	15·5	1·0470	35	1·0679	59	1·0744	83
1·0052	4	1·0228	16	1·0481	36	1·0685	60	1·0742	84
1·0060	4·5	1·0235	16·5	1·0492	37	1·0691	61	1·0739	85
1·0067	5	1·0242	17	1·0502	38	1·0697	62	1·0736	86
1·0075	5·5	1·0249	17·5	1·0513	39	1·0702	63	1·0731	87
1·0083	6	1·0256	18	1·0523	40	1·0707	64	1·0726	88
1·0090	6·5	1·0263	18·5	1·0533	41	1·0712	65	1·0720	89
1·0098	7	1·0270	19	1·0543	42	1·0717	66	1·0713	90
1·0105	7·5	1·0277	19·5	1·0552	43	1·0721	67	1·0705	91
1·0113	8	1·0284	20	1·0562	44	1·0725	68	1·0696	92
1·0120	8·5	1·0298	21	1·0571	45	1·0729	69	1·0686	93
1·0127	9	1·0311	22	1·0580	46	1·0733	70	1·0674	94
1·0135	9·5	1·0324	23	1·0589	47	1·0737	71	1·0660	95
1·0142	10	1·0337	24	1·0598	48	1·0740	72	1·0644	96
1·0150	10·5	1·0350	25	1·0607	49	1·0742	73	1·0625	97
1·0157	11	1·0363	26	1·0615	50	1·0744	74	1·0604	98
1·0164	11·5	1·0375	27	1·0623	51	1·0746	75	1·0580	99
1·0171	12	1·0388	28	1·0631	52	1·0747	76	1·0553	100
1·0178	12·5	1·0400	29	1·0638	53	1·0748	77	—	—

first one atom and then three atoms of hydrogen in the CH_3 group ; bromine acts similarly at 120°, but iodine does not react. It resists in the cold the action of chromic acid or permanganate, but when heated with the latter forms CO_2 ; it is very resistant to the action of reducing agents (sodium amalgam, &c.).

TESTS FOR ACETIC ACID. Better than by means of the specific gravity, the strength can be determined by means of a normal caustic soda solution (1 c.c. = 0·06004 grm. acetic acid), a *weighed* quantity being titrated and phenolphthalein used as indicator. When it contains more than 2 per cent. of water, it will no longer dissolve cedar-wood or turpentine oil. Metallic impurities are detected by diluting 10 c.c. of the acid to 100 c c., neutralising with ammonia and adding ammonium sulphide and ammonium oxalate , if the acid is pure, no alteration or precipitation should occur. If there is no sulphuric acid present, dilution with ten volumes of water and treatment with $BaCl_2$ in the hot will give no precipitate even after an hour's rest. In absence of hydrochloric acid, addition of nitric acid and silver nitrate gives no turbidity in the diluted acid. If no empyreumatic products are present, 5 c.c. of the acid diluted with 15 c.c of water will not decolorise 5 c.c. of an N/100-solution of permanganate even in fifteen minutes. For the detection of other organic acids and for other tests, *see* Notes on pp. 279 and 284.

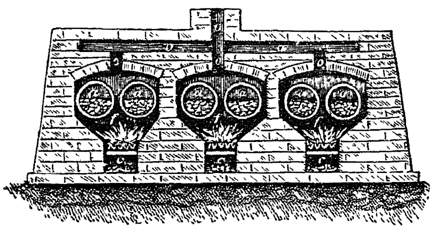


FIG. 229.

MANUFACTURE OF ACETIC ACID. The most important prime material for the manufacture of crude acetic acid is wood, alcohol (from cereals and wine) being only rarely used.

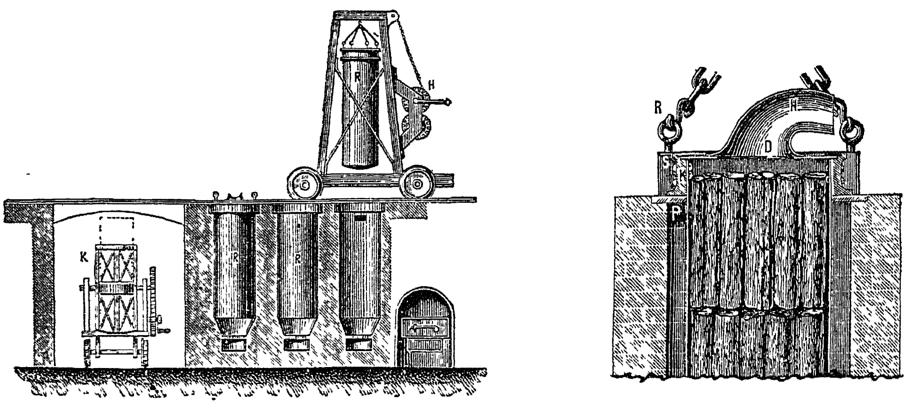


FIG. 230.

Dry Distillation of Wood. It has been already mentioned (*see* p. 36) that Lebon in 1799 patented a process of dry distillation of wood for producing illuminating gas and on p. 106, in dealing with the manufacture of methyl alcohol—also a product of the dry distillation of wood—the phases and crude products of this distillation out of contact of air were described. A description will now be given of the apparatus used in this industry. It is not necessary to consider the primitive furnaces formerly used, which gave a minimal yield and a slow and incomplete carbonisation, or the vertical retorts used in the early days of this industry, although these are again in use nowadays, but in a far more rational manner. These first vertical retorts were followed by horizontal ones, which are still used in many factories.

These are formed of sheet iron (10 to 12 mm. thick) and are about 1 metre in diameter and 3 metres in length ; they are arranged in pairs in furnaces (Fig. 229) with suitable flues for the hot gases, and they can be charged and discharged by means of hinges at

the back, although not very conveniently. On this account and also in order to obtain continuous working and hence more efficient utilisation of the heat of the furnaces, use is again being largely made of vertical retorts which can be removed from the furnace at the end of the operation, to be replaced immediately by other retorts already charged. In Fig. 230, on the left, is seen the arrangement of a battery of these retorts, with a trolley for raising and transporting the charged retorts, which are then emptied into the charcoal stove by means of the tipping trolley, K. The right-hand side of the figure shows in detail the upper part of a retort charged with wood. The capacity of each retort is about 4 cu. metres or 1500 kilos of wood; the smaller pieces are placed at the bottom, the medium-sized ones next, and the largest ones at the top. In order that the retorts may not be worn out too rapidly by the external heat, they are smeared with a very thin layer of earth made into a paste with water and applied with a brush. Every charge of 1500 kilos requires about 1000 kilos of coal for heating and distilling. If leaks are detected during the heating, they are closed with clay, and it is for this purpose that the retorts project 15 to 20 cm. beyond the furnace.

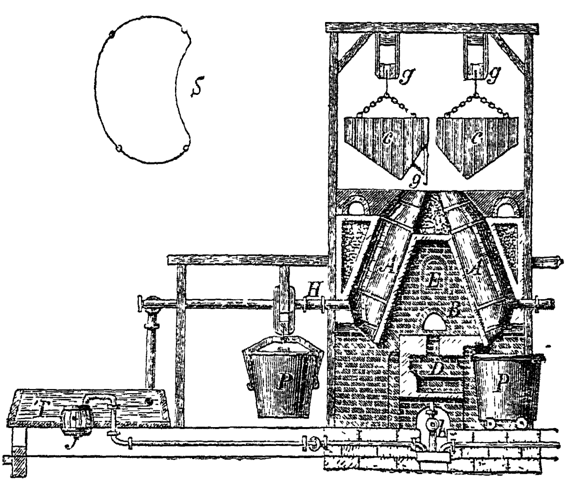


FIG. 231.

Although this arrangement is still largely used, it necessitates a considerable amount of manual labour and lifting, so that it has been proposed to incline the retorts as in gas-manufacture, and to furnish them with apertures at the top for charging and others at the bottom for automatically discharging them. Fig. 231 shows the section of a battery of these retorts (A) of the Mathieu type, S giving the cross-section of a retort. The wood is charged automatically from the running buckets, c, suspended at g. At the end of the operation the charcoal is discharged below into the vessel, P, which is provided with a cover to prevent the hot charcoal from igniting in the air. The vapours from the distillation pass into the tube, H, which conducts them into a coil cooled by the water in T and then into the barrel, J, where the tar and the pyroligneous acid separate; the gas, which does not condense but is still partly combustible, is washed and passes through the pipe, k, to be burnt under the furnace-hearth, D; there is no danger of explosion since, if there is any air in the retorts, it cannot communicate with the hearth, the barrel, J, serving as a water-seal.

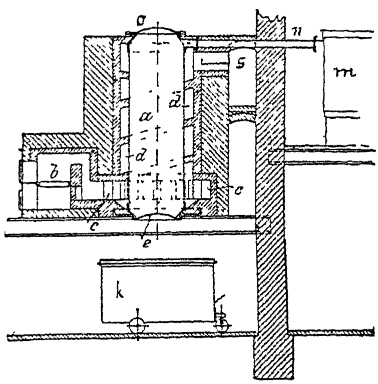


FIG. 232.

Of late years, use has also been made of vertical retorts (Fig. 232) with an upper orifice, o, for charging, and a lower one, e, for discharging (*see* Ger. Pat. 192,295, November 15, 1906). From the hearth, b, the hot gases pass to the flues surrounding the retort and thence at S to the shaft; the gases and vapours from the wood issue from the tube, n, and are partially condensed in the refrigerator, m. At the end of the distillation, the orifice, e, is opened and the charcoal discharged into the covered waggon, k, and conveyed to the store, whilst the retort, while still hot, is filled with a new charge of wood.

If the retorts are heated, not with coal, but by the gases produced with hot air in a regenerator furnace (*see* vol. i, pp. 367 and 501), one-third of the fuel is saved. Every

distillation lasts from 6 to 8 hours. The wood to be distilled is either stacked in piles for one or two years or dried in a warm chamber, which is placed near the retort furnaces and utilises hot gases which would otherwise be wasted. It is then cut into lengths, barked by hand or machinery, and divided longitudinally by circular saws or hatchets. The yield of acetic acid and by-products varies widely with the kind of wood. Preference is usually given to hard woods like oak, hornbeam, and beech; of less value are white woods, with the exception of lime, which gives good results; the wood of trees 18 or 20 years old, grown in a dry, poor soil and cut in winter, is more suitable than young wood or wood grown on plains in a moist or fertile soil and cut at other seasons of the year.[1]

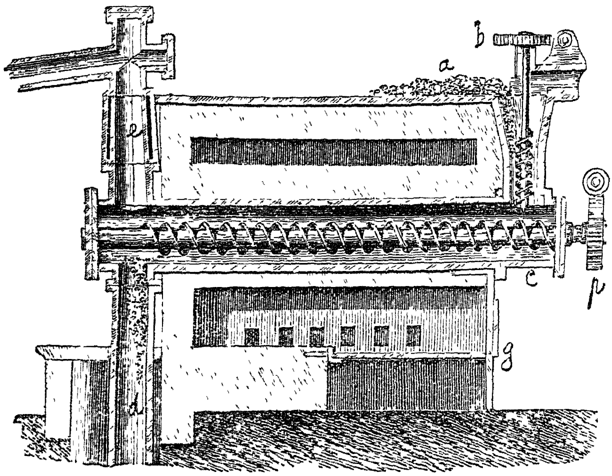


FIG. 233.

UTILISATION OF THE SAWDUST. Many attempts have been made, not always successfully, to utilise the various forms of wood refuse, especially the sawdust. But this presents considerable difficulty owing to the excessive moisture, the large volume, the abundance of resins which char and form incrustations, and the low thermal conductivity, which prevents the heat from reaching the middle of the retort.

[1] The yields obtained from 100 kilos of various kinds of wood, barked and subjected to rapid (*R*, about 3 hours) or slow distillation (*L*, more than 6 hours) are given below:

Kind of Wood	Tar	Aqueous acid distillate			Dry charcoal	Gas
		Total	Strength of acetic acid	Equal to pure acetic acid		
	Kilos	Kilos	Per cent	Kilos	Kilos	Kilos
Breaking buckthorn (*Rhamnus frangula*) branches *L*	7·58	45·21	13·38	6·05	26·50	20·71
Do. Do. . . . . . . *R*	5·15	40·23	11·16	4·49	22·53	32·09
Hornbeam (*Carpinus betulus*) trunk . . . *L*	4·75	47·65	13·50	6·43	25·37	22·23
Do. Do. . . . . . . *R*	5·55	42·97	12·18	5·23	20·47	31·01
Alder (*Alnus glutinosa*) trunk . . . *L*	6·39	44·14	13·08	5·77	31·56	17·91
Do. Do. . . . . . . *R*	7·06	40·70	10·14	4·13	21·11	31·13
Aspen (*Populus tremula*) trunk . . . *L*	6·90	40·54	12·57	5·10	25·47	27·09
Do. Do. . . . . . . *R*	6·91	39·45	11·04	4·36	21·33	32·31
Birch (*Betula alba*) trunk . . . . *L*	5·46	45·59	12·36	5·63	29·24	19·17
Do. Do. . . . . . . *R*	3·24	39·74	11·16	4·43	21·46	35·56
Beech (*Fagus sylvatica*) trunk. . . . *L*	5·85	39·45	11·37	5·21	26·69	21·66
Do. Do. . . . . . . *R*	4·90	45·08	9·78	3·86	21·90	33·75
Oak (*Quercus robur*) . . . . . . *L*	3·70	44·45	9·18	4·08	34·68	17·17
Do. Do. . . . . . . *R*	3·20	42·04	8·19	3·44	27·73	27·03
Austrian Pine (*Pinus laricio*) trunk . . . *L*	9·30	42·31	6·36	2·69	26·74	21·65
Do. Do. . . . . . . *R*	5·58	38·19	5·40	2·06	24·06	32·17
Pine (*Pinus abies*) trunk . . . . . *L*	5·93	40·99	5·61	2·30	25·55	28·11
Do. Do. . . . . . . *R*	6·20	40·15	4·44	1·78	23·35	32·80

A detailed study of the distillation of chestnut wood was made by G. Borghesani in 1910.

The bark and branches always give a smaller yield.

The plant of a small factory in Italy for distilling 100 quintals of wood per day would require a capital outlay of about £5600 (excluding the factory) for the purchase of a horizontal retort or cylinder taking four trolley-loads of 25 quintals each, a quenching drum, boilers, pumps, engines, copper coils, evaporating and rectifying apparatus, apparatus for the production of calcium acetate, methyl alcohol, acetone and tar, allowing 10 per cent for Customs duty and 10 per cent for erecting the plant and various other expenses.

The problem has not yet been definitely solved, but the forms of apparatus which up to the present have given the best results are that of Halliday (1851), shown in Fig. 233, and the more recent one shown in Fig. 234. Above the Halliday furnace the moist material (sawdust, exhausted dyewoods, &c.) is dried slowly in *a* and slowly descends a vertical screw moved by the cog-wheel, *b*, into the horizontal iron cylinder; there the mass is transported slowly to the opposite end by a horizontal screw and falls in a charred condition through the channel, *d*, into a water-tank, where it is extinguished. The vapours and gases from the distillation issue at *e* and pass to the condensing apparatus. The cylinder is heated by the hot fumes from the fire, *g*, several cylinders being heated at the same time in one furnace. In the other type of furnace (Fig. 234) the process is also continuous, the wood-waste being dried at *a*, and falling down outside a column formed of a number of superposed conical rings which occupy almost the whole of the interior of the cylinder, *b*; the gases from the distillation pass inside this column, the more volatile ones issuing from the tube, *c*, and the less volatile ones from the lower tube, *e*, all being passed along the pipe, *S*, to the refrigerator. The charred wood is discharged at *d*.

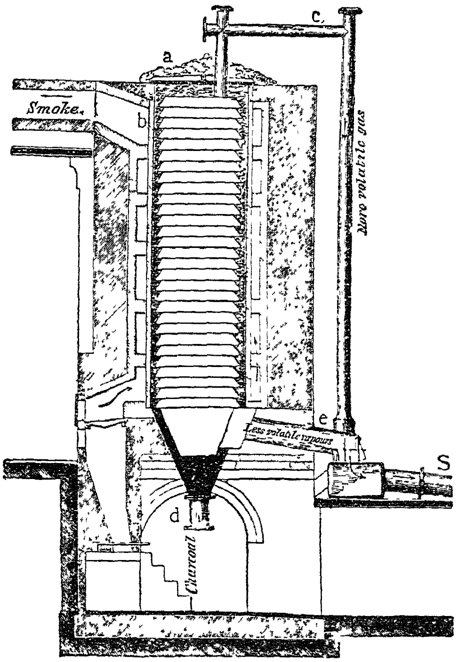


FIG. 234.

F. H. Meyer obtains better results by using two large retorts or cylinders set horizontally in a furnace. Into these cylinders run trolleys carrying metal plates with the sawdust spread out in thin layers. The fire is started and the first cylinder heated and distilled rapidly, the hot fumes then going to heat the second cylinder and so dry the sawdust, which is made ready for distillation, whilst the first cylinder is discharged and again charged with fresh sawdust. In Russia and America, large quantities of resinous woods are distilled, and these yield considerable amounts of resins and oils (of pine, turpentine, &c.) if superheated steam is used.

In 1905 the suggestion was made to distil wood in retorts in a current of chlorine so as to obtain acetic and hydrochloric (70 per cent. of the chlorine used) acids at the same time. Further, Larsen constructed rotating furnaces for the distillation of wood, and in 1904 the attempt was again made in Sweden to distil resinous woods with superheated steam so as to obtain an increased yield of turpentine.

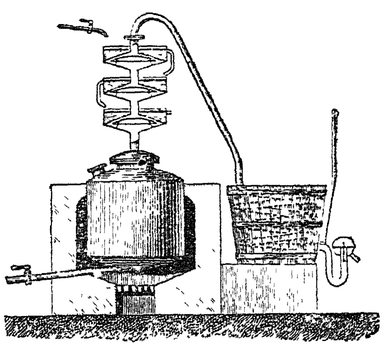


FIG. 235.

The liquid products from the dry distillation of wood are condensed in cooling coils and collected in large wooden vats. They consist mostly of an aqueous solution of acetic acid (about 5 to 8 per cent.), methyl alcohol (about 1 per cent.), and acetone (nearly 0·1 per cent.), and of small quantities of other acids (formic, propionic, butyric, valeric, caproic, &c.). On this liquid floats part of the tar, the rest of which collects at the bottom; the tar can be easily separated by decantation or by means of a centrifuge—such as is used for the separation of cream from milk—a low temperature and sometimes addition of a little tannin being used to facilitate the separation.[1] The aqueous solution,

[1] The *tar* is washed with water and heated to recover the acetic acid it contains, the tar thus obtained free from acid being used in the manufacture of rubber and of electric wires, its price being 8s. to 10s. per quintal.

which is brown, and has an unpleasant odour owing to the presence of empyreumatic products, can be treated in various ways according as crude acid or a purer acid is required. In the first case it is filtered through wood-charcoal, left to stand for a week to see if any further tar separates, and then distilled, in quantities of 800 litres, in a large copper still which has a capacity of 1200 litres (Fig. 235), is heated by direct-fire heat and is surmounted by three lenticular rectifying plates (Pistorius), the outer surfaces of these being cooled by running water. All the methyl alcohol and acetone first distil at 60° to 70°, their condensation being effected in the cooling coil ; when no more alcoholic liquid passes over (that is, when the density at 15° reaches the value 1·000) (about 100 litres), the temperature is raised to 95° and the acetic acid, which then begins to distil, is collected separately. To the 200 litres of aqueous, tarry matter remaining in the still, a further quantity of 700 litres of the crude pyroligneous acid is added, the alcoholic and acetic acid portions being again collected separately and the distillation continued until oily or tarry drops appear in the distillate ; a third charge is then added and the distillation carried out in the same way, the 200 to 300 litres of tarry matter left being then run off and a fresh distillation of three successive charges commenced.

The *acetic acid* thus obtained bears the name of *pyroligneous acid* and has a density of 1·013 ; it contains about 5 per cent. of the pure acid, has an intense empyreumatic

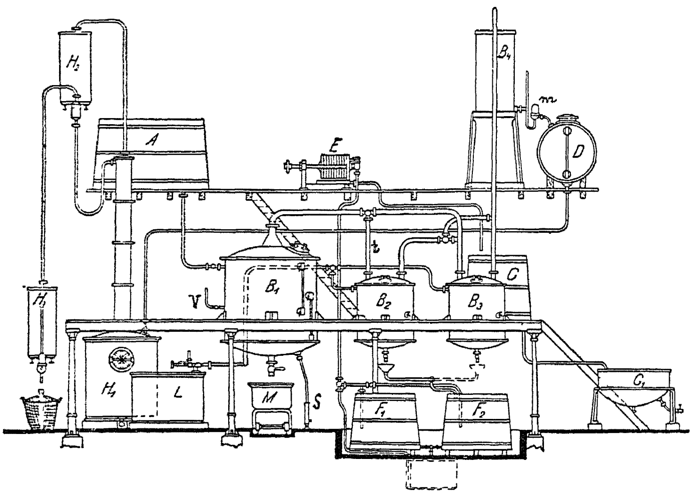


FIG. 236.

odour and rapidly turns brown in the air. None of the attempts made to purify and deodorise this product have given satisfactory results, and it is preferably purified indirectly by adding milk of lime until the reaction is alkaline, stirring well and allowing to stand until the tarry impurities collect on the surface or at the bottom and are hence easily separated by skimming and decantation.

The solution of calcium acetate is then evaporated to half its volume and treated with about 1 per cent. of hydrochloric acid to separate the final traces of tarry substances remaining dissolved. The liquid is then evaporated in shallow cast-iron pans heated with the hot gases from the wood-distillation furnaces (evaporation in a vacuum saves fuel and gives a better yield). The pasty calcium acetate which remains is heated to about 250° to decompose the tarry matters present, the heating being continued until a small portion of the mass gives a solution no longer showing a brown colour. For this, roasting continuous furnaces, similar to *Hasenclever's* apparatus for the preparation of calcium hypochlorite (*see* vol. i, p. 494), are used, a current of air at about 250° being passed in at the bottom of the apparatus in place of the chlorine. This procedure yields a commercial product containing 80 to 82 per cent. of pure *calcium acetate.* According to U.S. Pat. 927,135, 1909, white calcium acetate of high grade (86 to 92 per cent.) is obtained if the concentration and drying are carried out in a vacuum.

The separation of the various components of the crude pyroligneous acid and the simultaneous preparation of *calcium acetate* may also be effected by a process in which

three boilers are employed (Fig. 236). The crude, decanted pyroligneous acid is pumped into the large vat, A, from which it passes to the copper boiler, B_1 (3000 to 5000 litres), where it is boiled by means of steam-pipes (steam entering at V under 3 to 4 atmos. pressure and the condensed steam issuing at S). The vapours of acetic acid, methyl alcohol and acetone are passed through the tube, t, to the bottom of the second boiler, B_2 (1000 to 2000 litres), filled with milk of lime (from the lime-tank, L), which soon becomes heated nearly to boiling but retains the greater part of the acetic acid as calcium acetate, whilst the vapours proceed through the boiler, B_3, which also contains milk of lime; finally, the methyl alcohol and acetone vapours are condensed in the cooler, B_4, and collected in the reservoir, D, after passing through the test-glass, m, which indicates the density (*see* Fig. 129, E, p. 134, and Fig. 132, E, p. 136). The distillation goes on until the density reaches the value 1·00, this usually occurring when one-third or one-quarter of the total liquid of the boiler, B_1, is distilled. The first methyl alcoholic liquid which condenses, being more concentrated (30 to 40 per cent.), is kept and rectified apart from the remaining more dilute liquid by means of an ordinary rectifying column, H_1, H_2, H_3, in Fig. 236 (*see also* Fig. 138, p. 140).

The aqueous tarry residue left in B_1, after evaporation of all the acetic acid, is discharged into the movable tank, M.

When the liquid in the second boiler, B_2, assumes an acid reaction, the vapour from B_1 is passed into B_3, whilst B_2 is discharged into the vat, F_1, below, and again filled with milk of lime, into which the vapours from B_3 pass before they proceed to the condenser, B_4; a similar change is then made when the contents of B_3 become acid, and so on. The calcium acetate (about 20 per cent.) is pumped to the filter-press, E, and the clarified solution collected in the vat, C, which feeds the evaporating pans (iron or copper) which are fitted at the bottom with a lens-shaped jacket. This is best seen in Fig. 237; the steam for heating is passed in at a and the condensed steam runs off at b; f is a hood fitted with counter-weights, g, and hence capable of being raised, its object being to carry off the acrid, irritating vapours rising from the pan. More effective are pans with double concave bottoms. The concentration readily attains a value of 40 per cent.; the liquid then becomes pasty and must be stirred, this being continued until the mass will crumble between the fingers. The acetate is then lightly roasted at 125° to 145° on iron or copper plates heated by the hot gases from the pans or from the furnaces used for distilling the wood. By this means the mass loses the residual water and certain volatile tarry and empyreumatic products retained by the mass, which changes from brown to grey, if it is kept well mixed until it can be powdered between the fingers. The product is then broken up somewhat, and sold in bags holding 60 to 70 kilos. It contains 80 to 84 per cent. of pure calcium acetate,[1] 10 to 12 per cent. of water (half of which is lost only at about 150°), and 6 to 7 per cent. of impurities ($CaCO_3$, CaO, tarry matters, &c.).

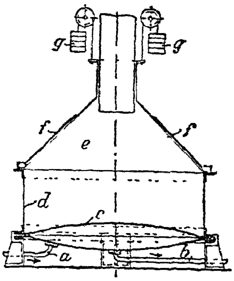


FIG. 237.

F. H. Meyer (Ger. Pat. 214,558, 1908) obtains calcium acetate free from phenolic compounds (which calcium acetate usually holds very tenaciously in the form of an emulsion) by passing the gases from the distillation of the wood—when freed from tar—into a tower containing lumps of calcium carbonate, which combines with the acetic acid but not with the phenols.

Also the fractional condensation method described in U.S. Pat. 969,635, 1910 (I. Heckel), although somewhat complicated, represents a marked improvement.

To obtain acetic acid from calcium acetate, the latter was formerly decomposed with hydrochloric acid. Nowadays, however, the decomposition is effected with concentrated

[1] The *strength of commercial calcium acetate* is determined by introducing a homogeneous sample of 5 grms. into a distilling flask with 50 c.c. of water and 50 c.c. of pure phosphoric acid (sp. gr. 1·2); the mixture is shaken and heated gently to avoid frothing, the distillation products being cooled and condensed. When the residue becomes dense, the distillation is continued in a current of steam. The distillation is continued until the distillate amounts to about 200 c.c.; this is then made up to 250 c.c. Part of this liquid is tested for hydrochloric and phosphoric acids and 50 c.c. of it are titrated with normal caustic soda solution with phenolphthalein as indicator to determine the amount of acetic acid; 1 c.c. of the normal soda solution corresponds with 0·079 grm. of calcium acetate. This titration also gives, besides acetic acid, traces of other volatile acids contaminating the calcium acetate, but this error is inevitable. Aqueous solutions of pure calcium acetate have the following densities: 5 per cent., 1·0330; 10 per cent., 1·0492; 15 per cent., 1·0666; 20 per cent., 1·0874; 25 per cent., 1·1130; 30 per cent., 1·1426.

sulphuric acid, the substances being mixed slowly in shallow iron pans arranged over a furnace and fitted with covers and stirrers : for 100 kilos of calcium acetate, 65 to 70 kilos of commercial sulphuric acid of 66° Bé. In order to avoid the formation of sulphur dioxide and other decomposition products at the high temperature attained initially and prevailing during the distillation, K. Linde distils in a vacuum with steam-heat (superheated if necessary); this procedure renders the operation more rapid and the acetic acid purer, besides reducing the consumption of sulphuric acid almost to the theoretical amount (60 kilos) and allowing of the treatment of larger quantities of material at a time ; further, the final portions of acetic acid, which are retained with great tenacity by the calcium sulphate, can be more easily and completely separated. The left-hand half of Fig. 238 shows diagrammatically the arrangement used in treating calcium acetate, when vacuum distillation is not employed. The sacks of calcium acetate, *a*, on the upper floor are tipped through a hopper on to the flat cast-iron pans, *b*, fitted with stirrers ; the pans are then closed and the measured amount of sulphuric acid in *n* (supplied from the large leaden tanks, *e*), slowly introduced. The mass, which begins to heat, is then heated by the fire underneath, the stirrers being kept in motion meanwhile.

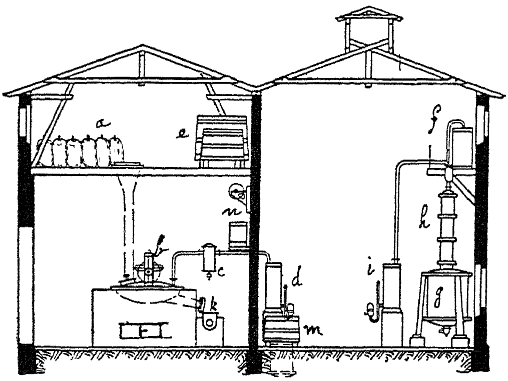


FIG. 238.

The acetic acid is gradually evolved from the copper tube leading first to the vessel, *c*, where the powder and acid spray carried over are deposited, and then to the copper coils in *d*, where the acetic acid is condensed and cooled, to be collected in the tank, *m*; a lateral test-glass, containing an aerometer, is fitted to the condenser and allows the density of the distilled acid to be read off at any moment. When the vapour-delivery tube begins to cool, the operation is at an end ; the fire is then covered with ashes and the residual calcium sulphate discharged through a wide lateral tube, *k*, and conveyed from the factory by an archimedean screw. Another distillation is then immediately commenced.

The yield from 100 kilos of calcium acetate amounts, under favourable conditions, to 80 kilos of 72 to 75 per cent. acetic acid, which always contains a few per cent. of sulphurous acid. Part of the latter has been already eliminated during the distillation as uncondensed gas and carried to the chimney. During recent years the introduction of vacuum distillation has been almost universal, as it economises fuel, gives an increased yield and a purer product, and accelerates complete distillation with a minimal production of sulphurous acid.

It will be readily understood that the use of less concentrated sulphuric acid and moist calcium acetate gives a more dilute acetic acid. A large part of the acetic acid is put on the market as it is or diluted with water to bring it to a concentration of 40 per cent., which is often required practically.

When, however, purer and more concentrated acid is desired, use is made of a rectifying column quite similar to those employed in the case of alcohol (*see* p. 140). The column is, however, constructed of copper, as this metal is more resistant (although not completely so) than others towards organic acids, if air is excluded. The heating is carried out with indirect steam under 5 atmos. pressure, which circulates in coils at the bottom of the still. The copper column is fitted inside with perforated plates of porcelain or baked clay arranged alternately with copper or clay rings ; the condenser consists of a copper, or, more rarely, a clay coil. The right-hand half of Fig. 238 represents the rectifying apparatus : *g* is the still, *h* the column, *f* the dephlegmator, and *i* the condenser. When the apparatus is not in use it is well rinsed and then completely filled with water, in order to prevent the acid, in presence of air, from attacking the copper. The first portion (about one-tenth) of the distillate is kept separate, as it is more dilute and contains the sulphurous anhydride and a large part of the empyreumatic products, and the last

tenth or more is not distilled but is also kept separate, being very impure. According as more or less foreshots and tailings are separated, a very concentrated (96 to 99 per cent.) acid, or one of about 80 per cent. strength is obtained, both, however, containing traces of copper and empyreumatic products ; the latter can be removed by mixing the acid in clay vessels with a little concentrated potassium permanganate and then filtering. The empyreumatic substances may also be removed (*e.g.* in the manufacture of essence of vinegar) by distilling the acid over potassium chromate. Traces of copper are eliminated by redistilling this acid from a copper still by means of indirect steam, the condensing coils and tubes being of earthenware or silver and carboys being used for collecting the pure, refined acid. Nowadays it is sometimes considered preferable to construct the small head of the still and the whole of the refrigerating coil of silver, as is shown in Fig. 239, since the coil then conducts heat well and is not much more expensive than the two earthenware coils necessary to give the same rapidity of condensation ; besides which, earthenware coils are fragile and of no value when broken.[1] According to Ger. Pat. 220,705, 1907, pure acetic acid containing only traces of SO_2 can be obtained by heating calcium acetate (100 parts) to 130° in a vacuum and then introducing a mixture (55 parts) of equal amounts of acetic and concentrated sulphuric acids ; by continuing the heating in a vacuum, the whole of the acetic acid, including that added, distils over, the yield being 95 per cent.

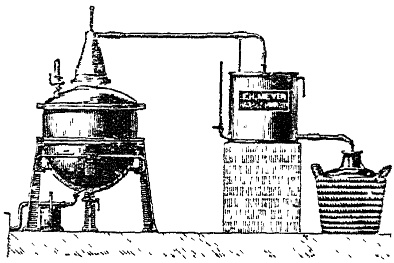


FIG. 239.

During the winter care must be taken not to cool the condensing coils too much, as otherwise the pure (glacial) acetic acid may solidify and cause obstruction. Also in stores where acetic acid is kept in wooden casks, earthenware vessels, or carboys, the temperature must be maintained above 16° if a troublesome solidification of large quantities of the acid is to be avoided. *Glacial acetic acid* is also prepared by distilling 92 parts of pure dehydrated (by fusion at 240°) sodium acetate with 98 parts of concentrated sulphuric acid. In 1901, the Renania chemical firm patented a process for distilling calcium acetate with a sodium polysulphate, $Na_2H_3(SO_4)_2$, which acts like sulphuric acid but without giving secondary decomposition *products*. Formerly, *glacial acetic acid* was obtained by *Melsen's reaction* (1844), which consists in adding potassium acetate to dilute acetic acid and evaporating until a salt, combined with acetic acid, crystallises ; this salt, which melts at 148°, decomposes at 200° to 250°, pure glacial acetic acid distilling and the potassium acetate (which decomposes only above 300°) remaining for a subsequent operation.

USES, STATISTICS, AND PRICE OF ACETIC ACID. Considerable quantities of commercial acetic acid (35–40 per cent.) are used in printing and dyeing wool and silk, especially with alizarin and other dyes which withstand feebly acid baths ; it is also largely employed for giving silk its characteristic rustling property after dyeing or cleaning. The pure acid serves in the preparation of numerous acetates (ammonium, chromium, and aluminium—which are used in dyeing tissues and rendering them impervious —lead, &c.), different esters and various aniline dyes. After it became obtainable in a pure state, by rectification, it acquired great importance for the preparation of essence of vinegar (various aromatic herbs being added) and, when diluted with water, replaces ordinary table vinegar. It has been proposed to denature acetic acid, to be used in chemical industries, by addition of formic acid, so that it may be freed from taxation (*see* p. 280).

[1] *Testing of acetic acid.* If no empyreumatic products are present, a mixture of 10 c.c. of the acid, 15 c.c. of water, and 1 c c. of 0 1 per cent. potassium permanganate solution will remain reddish in colour for more than one minute. The acid should not contain higher homologous acids ; these are detected by dissolving PbO (litharge) in the 30 per cent. acid until only a faint acidity remains, the solution being then heated and filtered ; if the crystals which form are not transparent and colourless, but show white flocks like mould, the acid is to be rejected. The presence of other organic acids in acetic acid can also be detected by fractionally precipitating the silver salt and determining the silver in the separate fractions by heating in a crucible. Pure silver acetate contains 64 6 per cent. of silver. For other tests *see* p. 272.

The price of the acid varies with the purity and concentration[1]; ordinary commercial 30 per cent. (sp. gr. 1·041) is sold at about 24*s.*; the 40 per cent. acid (sp. gr. 1·052) at 30*s.* to 32*s.*; and the 50 per cent. acid (sp. gr. 1·061) at 40*s.* per quintal. The pure acid costs 25 per cent. more than the commercial at the same concentration, and the pure glacial (99 to 100 per cent.) 88*s.* to 92*s.* per quintal.

There are four or five factories in Italy for the distillation of wood and the preparation of calcium acetate and acetone (one firm alone distils 300 quintals of wood per day), but they work irregularly, and in recent years calcium acetate has been imported from America. In 1910, 13,200 quintals were imported (all from the United States) at an average price of 19*s.* per quintal; in the same year 2212 quintals of the impure acid of less than 50 per cent. strength were imported at an average price of 22*s.* to 24*s.*, and 772 quintals of the pure acid of more than 70 per cent. strength at a price of 45*s.* to 72*s.* per quintal; also 861 quintals of crude acid and 1447 of pure dilute acid were exported.

In 1900 the United States produced 400,000 quintals of calcium acetate.[2] Germany obtained from wood in 1903 more than £280,000 worth of glacial acetic acid and exported about 35,280 quintals of greater strength than 30 per cent., this quantity diminishing to 28,453 quintals in 1905 and to 15,700 quintals in 1910 (also 1360 quintals less concentrated than 30 per cent.); 48,000 quintals of pyroligneous acid were imported for purification.

In 1900 the Badische Anilin- und Soda-Fabrik, Ludwigshafen, consumed, merely for the synthesis of artificial indigo (chloroacetic acid being prepared by means of liquid chlorine), more than 20,000 quintals of glacial acetic acid (corresponding with 100,000 cu. metres of wood), the total production of this acid in Germany being about 100,000 quintals.

Germany imported, in 1904, 182,000 quintals of calcium acetate; 205,100 quintals in 1905; 201,000 in 1906; 174,000 in 1908; and 235,450 in 1909; the production in the country did not exceed 100,000 quintals.

France distils every year the wood from 200,000 hectares of forest, obtaining 50,000 to 55,000 tons of distilled products of the value £600,000.

Importation to England was 3700 tons of acetic acid in 1909 and 4450 tons (£87,920) in 1910; also 3500 tons of calcium acetate in 1909 and 4300 tons (£42,470) in 1910. The United States exported 30,000 tons (£306,000) of calcium acetate in 1910 and 35,000 tons (£318,600) in 1911.

The manufacture of crude pyroligneous acid in Italy is exempt from taxation, but the rectification and production of the pure acid are subject to a manufacturing tax of 12*s.* per quintal for acid of less than 10 per cent. strength; 41*s.* for 10 to 30 per cent. acid; 72*s.* for 30 to 50 per cent. acid; 100*s* for 50 to 75 per cent. acid; 129*s.* for 70 to 90 per cent. acid; and 144*s.* for stronger acid. The Customs import tariff adds a further tax of 19*d.* per quintal for crude pyroligneous acid of less strength than 50 per cent., and for the pure acid up to 10 per cent.; 4*s.* 10*d.* for 10 to 30 per cent. acid; 8*s.* for 30 to 50 per cent. acid; 11*s.* for 50 to 70 per cent. acid; 14*s.* for 70 to 90 per cent. acid; and 16*s.* for 90 to 98 per cent. acid.

MANUFACTURE OF VINEGAR

Vinegar is formed by the acetic fermentation (by means of *Mycoderma aceti, Bacillus aceticus*, or *Bacterium aceti*, *see* p. 122, Fig. 114, *a*) of saccharine liquids which have undergone alcoholic fermentation, such as wine, beer, cider, &c. Since this transformation of alcohol into acetic acid takes place merely on exposure of these liquids to the air, it is

[1] The balance-sheet for a small factory treating 10 quintals of calcium acetate per day is roughly as follows:
Outgoings 10 quintals of 80 per cent calcium acetate, 350 lire + 500 kilos of coal for decomposing the acetate, for the first and second distillations, for rectification and for generating steam, 20 lire + 6 5 quintals sulphuric acid (66° Bé), 41 lire + staff and general expenses, insurances, &c, 40 lire + depreciation on machinery (50,000 lire) and buildings (40,000 lire), 25 lire + lubrication, lighting, repairs, &c, 18 lire + motive power 8 lire . . . . . . Total 502 lire
Income · 450 kilos of 98 per cent. acetic acid, 450 lire + 300 kilos 30 per cent. acetic acid, 85 lire. Total 535 lire.
Capital employed (circulating as well), 120,000 lire; net annual profit, about 12 5 per cent.

[2] In 1907 the United States contained 100 distilleries treating a total of 4,390,000 cu metres of wood (1,767,000 cu. metres in 1900) with a mean yield per cubic metre of 8 to 10 litres of methyl alcohol (82 per cent), 22 to 25 kilos of calcium acetate (80 to 82 per cent.), 15 to 20 litres of tar, and 0 5 cu. metre of charcoal, 0 6 cu. metre of wood being used as fuel for heating the retorts The best yields are obtained with maple-wood, then follow beech, birch, and the Coniferæ (which form only 10 per cent of the total wood distilled). The numerous sawmills of the United States yield 150 million tons of waste.

probable that vinegar and hence acetic acid was the first acid known to man. The same result is obtained by treating alcohol with various oxidising agents (chromic acid, ozone, manganese dioxide and sulphuric acid, &c.), but acetaldehyde is also largely formed in these cases, which hence do not compete in practice with the biological process. The composition of vinegar was studied by Berzelius (1814), and Kutzing in 1837 showed the importance of the living organism of the mother-of-vinegar to the formation of acetic acid, while Turpin in 1840 examined and characterised these micro-organisms more exactly. According to Liebig, the transformation of alcohol into acetic acid is brought about by the catalytic action of certain nitrogenous substances capable of fixing oxygen from the air and of yielding it to the alcohol. In 1868, however, Pasteur showed that this phenomenon is caused by a vegetable organism, *Mycoderma aceti*, formed of small, oblong cells (about 3 micro-mm. long), slightly constricted in the middle (where segmentation then takes place) and often arranged in chains. When these multiply at the surface of the alcoholic liquid, they form first a thin membrane which gradually thickens, and when this membrane is formed in the body of the liquid it becomes mucilaginous and spreads through the whole liquid, giving a compact mass—the so-called *mother-of-vinegar*—reaching to the surface. It develops very well in slightly alcoholic liquids (3 to 6 per cent., but better with 13 per cent. of alcohol, and still more readily in presence of about 1 per cent. of acetic acid and 0·1 per cent. of phosphate); the most favourable temperature is about 30 per cent., acetification ceasing at 45° and below 5°; the action is retarded by light. When the acetic membrane becomes submerged, the fermentation ceases and only recommences with the formation of a fresh superficial membrane, which can absorb oxygen from the air and transfer it to the alcohol [1]:

$$CH_3\cdot CH_2\cdot OH + O_2 = H_2O + CH_3\cdot COOH.$$

According to this equation, the theoretical yield is 60 grms. of acetic acid per 46 grms. of alcohol, but the practical yield is 15 to 20 per cent. less than this; under the most favourable conditions, a liquid containing 10 per cent. of alcohol by *volume* yields a vinegar with 10 per cent. of the acid by *weight*. When almost all of the alcohol is converted into acetic acid, part of the latter begins to decompose into $H_2O + CO_2$; this change can be avoided by continuing to add alcohol to the acetic liquid or by causing the mother-of-vinegar to sink, and decanting the liquid. The old or slow wine-vinegar process, known as the *Orleans process*,[2] has been replaced almost everywhere by the more rapid *German process*, proposed by Schützenbach in 1823 and subsequently greatly improved. But as early as 1730 Boerhave prepared vinegar—and in some places his method is used even to-day—by means of two vats standing on feet and communicating at the bottom by means of a tube. One vat is filled with the wine, but the other is only

[1] This explains the harmful effect of *vinegar worms* (small worms belonging to the Nematodes), which form a transparent, white, slimy mass moving along the walls of the vessel, and breaking the skin of *Mycoderma aceti* at the surface of the liquid and hence causing it to sink. Another enemy of vinegar is the *vinegar mite* (an insect ¼ mm in length) which multiplies at an enormous rate and accumulates in large masses in the vinegar, succeeding in interrupting the acetic fermentation and starting putrefactive changes. In order to prevent the entry of these insects into the vats and casks, the latter are smeared outside with a ring of birdlime, to which the mites become fixed. Also *Mycoderma vini* hinders the development of *Mycoderma aceti*, and equally harmful to acetic fermentation are antiseptic substances in general, sulphur dioxide and empyreumatic substances (including those of pyroligneous acid). Blue and violet light (hence white light, but not red or yellow light) likewise retard the growth of *Mycoderma aceti.*

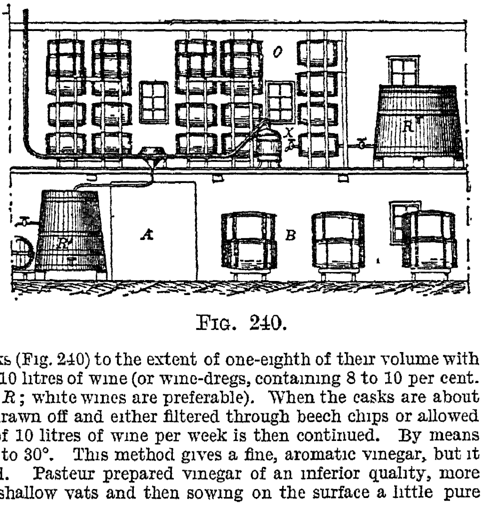


FIG. 240.

[2] This process is one of the oldest and was formerly, and is still, carried out more especially in the town of Orleans, by filling a number of superposed casks (Fig. 240) to the extent of one-eighth of their volume with good wine vinegar and then adding each week about 10 litres of wine (or wine-dregs, containing 8 to 10 per cent. of alcohol, filtered through beech shavings in the vat, *R*; white wines are preferable). When the casks are about half-full, the vinegar is made and two-thirds of it is drawn off and either filtered through beech chips or allowed to deposit in the vat, *R'*, underneath; the addition of 10 litres of wine per week is then continued. By means of the stove, *X*, the temperature is maintained at 25° to 30°. This method gives a fine, aromatic vinegar, but it is very slow and cannot be interrupted when desired. Pasteur prepared vinegar of an inferior quality, more rapidly by adding a little vinegar to wine in wide, shallow vats and then sowing on the surface a little pure *Mycoderma aceti* from another vat.

about half filled, the vinasse not being submerged. Every twelve hours the full vat is half emptied into the other. If the temperature is kept at 25° to 30°, acetification is complete in 12 to 15 days.

In the German or *quick vinegar process*, wooden vats, 2·5 to 3 metres high and 1·5 to 2 metres in diameter, are used (Fig. 241). These are filled almost completely with wood shavings, which are supported on a perforated false bottom, *L*, and covered with a wooden disc with perforations traversed by cords held by knots so as to form a uniform spray of the alcoholic liquid (8 to 10 per cent.), mixed with one-fifth of its volume of wine-vinegar, over the wood chips. Six or seven glass tubes passing through the upper disc allow of a continuous circulation of air, which enters at the periphery of the lower part of the vat through the holes, *Z*, and through the pipe, *R*, passes through the shavings—which become gradually warmed as acetification proceeds—and issues through the apertures, *Z'*, at the top. The temperature is shown by a thermometer, *T*, inserted in a glass tube, reaching to the middle of the vat. When the temperature exceeds 40°, it is lowered by a more rapid passage of the alcoholic liquid, which collects at *E*, and is discharged by the siphon, *H*, to be conveyed to the top of the vat and again circulated through the shavings, this process being continued until acetification is complete. In some cases three such vats are superposed, the liquid passing down through them all; after one or two complete circulations the operation is complete, although the amount of acid formed is not equal to that of the alcohol in the original liquid.

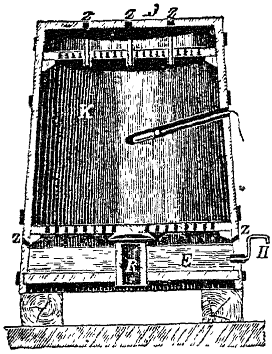


FIG. 241.

The liquids thus obtained contain up to 12 to 13 per cent. of acetic acid (14 per cent. cannot be exceeded as the *Mycoderma* would then be killed) and, if the operations are conducted with care, less than 10 per cent. of the alcohol used is lost; otherwise, especially if the temperature becomes too high, so that part of the alcohol evaporates, the loss may amount to 30 to 50 per cent.

Vinegar of an inferior quality is largely prepared nowadays from various alcoholic liquids made from cereals, starch, beetroot, or molasses, just as industrial alcohol is prepared. But such vinegar lacks the pleasant aroma of wine-vinegar.

It has been proposed to accelerate acetification by means of compressed air, but greater success has attended the *Michaelis* or *Luxemburg method*, in which acetification is carried out in rotating casks (5 to 6 hectols.) filled with beech shavings (washed first with hot water and then with hot vinegar) and traversed by two osier tubes, one along the horizontal axis and the other along the vertical axis, to allow of the circulation of air. The shavings are washed with wine-vinegar, and the cask filled about half full with wine (Fig. 242). During the first three days the casks are rotated three times a day and subsequently six times a day. Acetification is complete in about eight days.

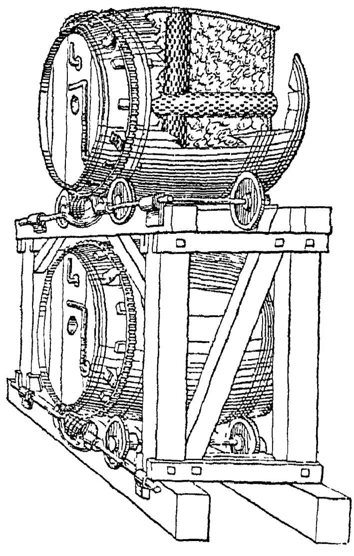


FIG. 242.

An ingenious, rapid, and continuous method for the manufacture of vinegar is that of Villon (Fig. 243), which makes use of two drums (2 metres by 2 metres), *B B*, arranged inside in the form of a spiral. The iron spirals are covered or varnished with gutta-percha and are 30 metres in length, the coils being 10 cm. apart and the spaces between filled with beech shavings or charcoal. The drums rotate in opposite directions, the left-hand one rotating once in five minutes and dipping up each time 8 litres of the alcoholic liquid from the vessel, *C*, this liquid being then passed through the axial tube to the second drum, which discharges it into the other dish, *C*. The liquid then passes to a similar

pair of drums and thence to a third pair, on leaving which the vinegar is ready; by this means 1000 litres are produced in 20 hours. By means of the pump, *R*, a current of air is drawn through each drum to the centre, whence it passes through the tube, *V*, to a cooling coil, *S*, to condense the small amount of acetic acid vapour it carries over.

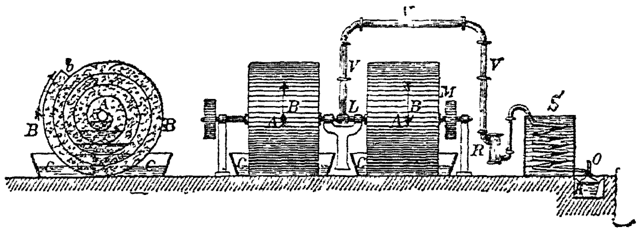


FIG. 243.

Another continuous and very rapid method, which avoids loss of acetic acid or aldehyde and diminishes the labour necessary by establishing more intimate contact between the alcoholic liquid and the subdividing material, is that in which the *stave acetifier* (Figs. 244 and 245) is used. This consists of a wooden box, *P*, about 1 metre wide and 2 metres high, terminating at the top in a channel, *R*. The box is filled with nine or ten layers of thin beech sticks placed vertically and very close one to the other. The position of the sticks in one layer is crossed with respect to that of the sticks in the next layer. These sticks are held apart by small strips of wood so as to allow of the passage of a thin film of liquid downwards and of the air upwards. The total surface of the sticks in an apparatus of the dimensions stated above amounts to more than 1000 sq. metres, so that the oxidation is extraordinarily rapid, while the working, which may continue uninterruptedly for years, is extremely regular and simple. The air enters at a lateral slit, *Z*, at the bottom, this being covered with gauze to prevent access of harmful insects; and the draught is regulated by a slider in the exit-channel, *R*; the vinegar is discharged at *E*. The thermometer, *T*, shows the temperature of the air as it leaves. The figure shows also the contrivance for feeding the apparatus regularly and continuously with the alcoholic liquid. The latter is contained in the tank, *B*, in which is a wooden float, *F*, moving along three vertical rods, *L*, and carrying the glass siphon, *W*, terminating in a rubber tube with a regulating clip, *n*. The liquid from the siphon falls into a tube, *G*, and thence through the tube, *A C*, to the vessel, *H* (3 litres capacity), and, when this is full, it discharges through the siphon, *r*, on to the perforated plate, *V*, which distributes the liquid as a fine spray over the bundles of sticks, and is traversed by several glass tubes to allow of the escape of the ascending air. In this way the flow of liquid from *B* is independent of the amount of liquid present in it at any instant (that is, of the pressure it exerts). The clip, *n*, is regulated so that the vessel, *H*, is refilled and discharges its 3 litres of liquid every one or two hours (or in any other prearranged time).

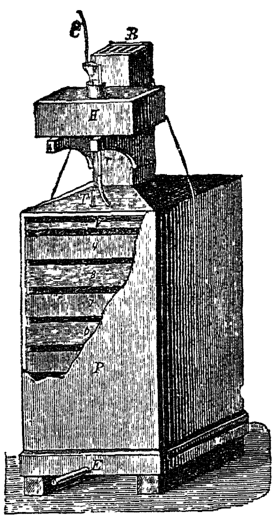


FIG. 244.

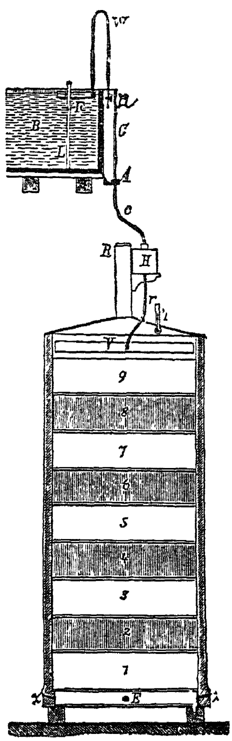


FIG. 245.

Attempts have been made to replace the ordinary biological acetification by chemical oxidation of the alcohol by means of platinum black or even of ozone, but neither method has attained to practical importance.

Vinegar is kept in *full* casks in stores like those used for wine, but it is not injured by a high air-temperature. An excess of air in the vessels and the continued presence of the mother-of-vinegar lower its strength, and, when this becomes too low, putrefaction may develop. Its keeping properties and aroma may be enhanced by pasteurisation (*see* p. 156) at 50° to 60°. A weak vinegar may be strengthened and kept if a little *pure* acetic acid is added to it.

WINE VINEGAR (white or red) is distinguished from other vinegars by its aroma, due partly to ethyl acetate and to small proportions of aldehydes. It usually contains 6 to 9 per cent. of acetic acid and less than 1 per cent. of alcohol, and has the density 1·015 to 1·020. The extract and the ash have the same compositions as those of wines, the former being rich in cream of tartar.

BEER VINEGAR contains 4·5 to 6 per cent. of extract rich in maltose, dextrin, albuminoids, and phosphates, and exempt from cream of tartar.

This vinegar also contains less acetic acid and, since it does not keep so well as that from wine, is used to break down excessively strong vinegars.

ARTIFICIAL VINEGARS, prepared from purely alcoholic liquids or from acetic acid and a colouring material such as caramel, have very little extract and no cream of tartar, whilst the percentage of acetic acid sometimes reaches 12 or 13.

In the ANALYSIS OF VINEGAR, the density of the extract and the ash are determined as with wine (p. 156). The content of acetic acid cannot be estimated exactly with a standard alkali solution, since other acids (tartaric, succinic, &c.) present influence the titration; nor do the graduated tubes (*acetometers*) give accurate results. A more exact determination is effected by distilling the acetic acid in a current of steam, as in the analysis of calcium acetate (p. 277).

Adulteration of vinegar, which is somewhat frequent, is detected by the following tests: real wine vinegar exhibits certain relations between the acetic acid and extract. In wine the ratio is 4 parts of alcohol for about 1 of extract, after deduction of the sugar present in sweet wines; assuming a loss of 15 per cent. of the alcohol during the conversion into vinegar, a pure wine vinegar with 5·31 per cent. of acetic acid should contain 1·08 per cent. of extract; one with 7·15 per cent. of acid, 1·44 per cent. of extract; one with 8·9 per cent. of acid, 1·8 per cent. of extract, and one with 10·7 per cent. of acid, 2·16 per cent. of extract, the ratio of acid to extract always being about 4·9 : 1. Addition of malt or beer vinegar is recognised by its reduction of Fehling's solution, or by concentrating 80 c.c. of the vinegar to about 2 c.c. and then adding alcohol: the formation of a white precipitate (dextrin) soluble in water indicates such adulteration with certainty.

If mineral acids have been added, 4 or 5 drops of a dilute alcoholic solution of methyl violet (1 : 10,000) will give a greenish colour with 25 c.c. of the vinegar; also, with zinc sulphide, hydrogen sulphide is evolved; and, finally, after the vinegar has been heated with a trace of starch, it will not give a blue colour with iodine. The presence of sulphuric acid in vinegar is detected by the white precipitate formed with barium chloride, hydrochloric acid by that given by silver nitrate and oxalic acid by the formation of a white precipitate with calcium chloride.

Artificial colouring-matters are detected in the same way as in wine and beer, and pyroligneous acid by the furfural reaction (*see this*).

The *price* of good wine vinegar is little less than that of wine, but artificial vinegars are cheaper.

France produces annually 600,000 to 700,000 hectols. of vinegar, but in Italy the production is much less owing to the competition of artificial vinegar and to the excessive duty of 17*s*. 6*d*. per hectol.; in 1904–1905 the thirty-eight Italian vinegar factories consumed 6160 hectols. of alcohol, the output of artificial vinegar being 60,000 hectols.

DERIVATIVES OF ACETIC ACID

SALTS OF ACETIC ACID. These are termed acetates, and are all soluble in water (the least soluble are silver and mercurous acetates). They are readily formed by neutralising acetic acid with metallic oxides or carbonates, previously dissolved in water. But pure anhydrous acetic acid or its alcoholic solution does not decompose alkaline carbonates, so that CO_2

precipitates potassium carbonate from an *alcoholic* solution of potassium acetate, acetic acid being liberated.

Even in aqueous solution, acetic acid undergoes only slight dissociation, but the acetates are considerably dissociated and diminish the dissociation and hence the acid characters of acetic acid (*see* vol. i, p. 94).

POTASSIUM ACETATE (Normal), $CH_3 \cdot COOK$, melts at 229° and is soluble in water or alcohol. It is obtained by neutralising potassium hydrogen carbonate ($KHCO_3$) solution with acetic acid and evaporating to dryness. The *acid acetate*, $CH_3 \cdot COOK$, $C_2H_4O_2$, is obtained by dissolving the normal acetate in acetic acid and separates from the latter in crystals which melt at 148° and decompose at 200°, liberating anhydrous acetic acid.

A Diacid Potassium Acetate, $CH_3 \cdot COOK$, $2C_2H_4O_2$, melting at 112°, is also known.

The commercial refined normal acetate costs £6 per quintal.

SODIUM ACETATE, $CH_3 \cdot COONa$, crystallises from water with $3H_2O$, melts at 100°, loses water and solidifies at a higher temperature and then melts only at 319°.

In the cold it dissolves to some extent (1 : 23) in alcohol or in its own weight of water, giving a feebly alkaline solution and considerable lowering of temperature.

It is prepared by neutralising pyroligneous acid almost completely with sodium carbonate and concentrating the solution (after removal of the tar from the surface) to 27° Bé.; the crystals which separate on cooling are centrifuged, but are always reddish brown. The mother-liquors (which readily become mouldy) are taken to dryness and lightly roasted to burn the tarry products. Crude sodium acetate is preferably prepared by treating calcium acetate with sodium sulphate and then with a little soda to precipitate all the lime; the filtered or decanted solution is evaporated to dryness, heated to 250°, redissolved in water, concentrated, and allowed to crystallise.

According to C. Bauer, pure sodium acetate, free from the reddish brown colour, can be prepared directly from pyroligneous acid by neutralising with sodium carbonate, and adding to the solution concentrated to 27° Bé., 2 per cent. of caustic soda, the liquid being then allowed to crystallise in wide and shallow wooden vessels. The crystals are separated by centrifugation and redissolved, the small amount of free caustic soda being then neutralised with commercially pure acetic acid; the solution is boiled to expel the excess of acetic acid, concentrated to 27° Bé., and left to crystallise.

Acid sodium acetates are also known.

Sodium acetate serves for the preparation of pure acetic acid, and is used in dyeing, &c.

Crude red sodium acetate is sold, according to its degree of purity, at 28*s*. to 30*s*. per quintal; the white purified crystals (pharmaceutical) at 48*s*. to 56*s*.; and the doubly refined and fused anhydrous product at 104*s*.

AMMONIUM ACETATE, $CH_3 \cdot COONH_4$, is obtained by neutralising hot glacial acetic acid with a current of dry ammonia or with ammonium carbonate. The pure crystals which separate melt at 113° to 114° and, although not highly hygroscopic, dissolve readily in water giving an alkaline solution; the solution in acetic acid deposits the acid acetate melting at 66°. The salt acts as a sudorific and dissolves lead oxalate and sulphate. It is used to some extent in dyeing.

The commercial brown solution at 10° Bé. costs £2 per quintal and the pure solution of the same density 49*s*. 6*d*.; chemically pure crystals cost £10 per quintal.

CALCIUM ACETATE, $(CH_3 \cdot COO)_2Ca + 2H_2O$. The preparation of the commercial product has already been described on p. 276. The pure salt is obtained by repeated crystallisation from water, and costs up to 96*s*. per quintal. Its solubility in water diminishes with rise of temperature up to a certain point and subsequently increases.

FERROUS ACETATE (Pyrolignite of Iron), $(CH_3 \cdot COO)_2Fe$. The crude product, used as a mordant in the dyeing and printing of textiles, is obtained from pyroligneous acid and iron filings, or from calcium pyrolignite and a concentrated solution of ferrous acetate; the tarry substances present preserve it from oxidation. A solution of 20° Bé. costs 12*s*. per quintal and one of 30° Bé. 17*s*. 6*d*. The pure product is prepared by dissolving freshly prepared ferrous hydroxide in 30 per cent. acetic acid.

FERRIC ACETATE, $(C_2H_3O_2)_3Fe$, used as a mordant in dyeing, is obtained from the ferrous salt and sodium acetate. It gives a reddish brown solution in the cold, but in the hot and in presence of a large amount of water, a reddish brown mass of basic ferric acetate, $Fe(C_2H_3O_2)_2OH$, separates; it is this which fixes the colouring-matters.

ALUMINIUM ACETATE (Normal), $Al(C_2H_3O_2)_3$, is obtained from aluminium sulphate and the corresponding quantity of lead acetate. It is known only in solution, in which it gradually undergoes spontaneous decomposition into acetic acid and the basic acetate: $Al(C_2H_3O_2)_3 + H_2O = Al(C_2H_3O_2)_2OH + C_2H_4O_2$.

When the solution of the basic acetate is boiled, aluminium hydroxide and acetic acid separate: $Al(C_2H_3O_2)_2OH + 2H_2O = Al(OH)_3 + 2C_2H_4O_2$.

It is used in dyeing, in the printing of textiles and in the preparation of *impermeable fabrics*. For the last purpose, the material is first soaked in aluminium acetate solution and then heated or steamed, $Al(OH)_3$ thus being deposited in the pores of the fabric, which is rendered impervious to water.

BASIC ALUMINIUM ACETATE, $Al(C_2H_3O_2)_2OH + 1\frac{1}{2}H_2O$, is obtained crystalline by evaporating a solution of the normal acetate cautiously at a temperature not exceeding 38°; it is soluble in water. Dilute solutions (4 to 5 per cent.) of the normal acetate gradually deposit, on the walls of the containing vessel, a porcelain-like crust of a basic acetate with $2H_2O$ or $2\frac{1}{2}H_2O$: this is insoluble in water.

It is used, like the normal salt, in dyeing, textile-printing, &c.

SILVER ACETATE, $C_2H_3O_2 \cdot Ag$, is obtained crystalline by adding silver nitrate to a concentrated solution of an acetate (*e g.* that of ammonium). It is a characteristic salt crystallising from water in shining needles (solubility 1 : 100 at 20°, 2·5 : 100 at 80°). When calcined in a porcelain crucible, it leaves, like all organic silver salts, pure metallic silver.

NORMAL LEAD ACETATE (Sugar of Lead), $(CH_3COO)_2Pb + 3H_2O$, forms monoclinic plates or crystals, has a disagreeable, sweetish taste, is poisonous and exhibits a faintly acid reaction. It is slightly soluble in alcohol and more so in water (1 part dissolves in 1·5 part of water at 15°, in 1 part at 40°, or in 0·5 part at 100°). It loses the water of crystallisation over sulphuric acid or at 100° and then melts above 200°.

It is used as a mordant in the dyeing and printing of textiles and also in the preparation of various lead salts and paints and certain pharmaceutical products; further, for conferring hot-drying properties on linseed oil to be used for varnishes.

Italy produced 450 quintals in 1904, 800 in 1906, and 1400 (worth £3680) in 1908. Germany exported 17,655 quintals in 1905 and 20,780 (worth £52,000) in 1906.

The refined crystalline product is sold at 48*s.* to 56*s.* per quintal, and the chemically pure at 72*s.*

It is best prepared commercially by the Bauschlicher-Bauer method (1892–1905) from commercial pure 60 per cent. acetic acid (*see* Tests on pp. 272 and 279) and pure litharge containing 99 per cent. of PbO.[1] A pitch-pine vat is fitted with a tight cover with three apertures: the central one for the shaft of a wooden stirrer, another for a copper cooling coil to condense the acetic acid vapours, and the third for the neck of a large wooden hopper, by means of which the litharge is dropped on to a wooden distributing roller provided with teeth and placed under the lid. The required quantity of acetic acid is heated to 60° by a copper steam coil in the bottom of the vat, and the litharge gradually added in the proportion of 103 kilos per 100 kilos of 60 per cent. acetic acid; each 100 kilos added require about an hour to dissolve if the stirrer is kept in motion and the temperature does not exceed 65°. The solution has a density of 70° to 72° Bé. and, if it does not show an acid reaction, it is slightly acidified with acetic acid,[2] and the mother-liquor (35° to 37° Bé.) from a preceding operation added in such amount that the density becomes 50° to 52° Bé. The solution at 65° is then allowed to clarify in a couple of tightly closed wooden vats, each fitted with a horizontal rail carrying strips of lead dipping into the liquid so as to remove the small amount of copper present. After 5 to 6 hours the solution is passed through a cloth filter-press with wooden channels, and is then left to crystallise in wooden vessels for 8 to 10 days—until the density

[1] It should contain neither iron, which would colour the crystals, nor aluminium, which would render filtration difficult.

[2] The subsequent crystallisation is rendered difficult if the solution contains basic acetate, the presence of this being inferred from the turbidity produced on mixing a little of the liquid with an equal volume of 1 per cent. corrosive sublimate solution.

of the mother-liquor falls to 35° Bé. in winter or 37° in summer. After the liquid has been decanted, the mass of small crystals (more concentrated and hotter solutions give larger crystals) is treated in a copper centrifuge and dried in wooden boxes placed in a vacuum apparatus at a temperature not exceeding 30°.[1]

MONOBASIC LEAD ACETATE (Subacetate of Lead), $(C_2H_3O_2)_2Pb + PbO + H_2O$, and **Dibasic Lead Acetate**, $(C_2H_3O_2)_2Pb + 2PbO$, are obtained by melting the normal acetate with a greater or less proportion of litharge (3 : 1 for the monobasic salt) on the water-bath; the former is readily soluble and the latter only slightly so (1 : 18 at 20° and 1 : 5·5 at 100°) in water. The *lead acetate of the pharmacopœia* is a 2 per cent. solution of the monobasic salt, and is used as a medicine, for weighting silk, for decolorising vegetable juices, and for preparing white-lead and aluminium acetate. The anhydrous salt costs 104*s*. per quintal.

NORMAL CHROMIC ACETATE, $Cr(C_2H_3O_2)_3 + H_2O$, is obtained from calcium or lead acetate and chrome alum or chromic sulphate. It gives a violet solution, which becomes green, without decomposing, when heated.

Basic Chromium Sulphate is obtained in a similar way from basic chromium sulphate or by adding ammonia or sodium hydroxide or carbonate to a solution of the normal acetate. The basicity increases with the amount of alkali, the compound $Cr_2(C_2H_3O_2)_5OH$, being gradually converted into $Cr_2(C_2H_3O_2)_2(OH)_4$ or even more basic salts still. The more basic the acetate the more will it decompose on boiling and the more readily it will serve as a mordant in dyeing or, better, in printing, since the reducing action of the textile fibres or of the colouring-matters or of other organic substances added, results in the separation of the true mordant, $Cr(OH)_3$, which forms stable lakes with the dyes (alizarin, hematin from log-wood, &c).

Commercial chromium acetate solutions at 20° Bé. are sold at 32*s*. per quintal, those of 40° Bé. at 56*s*., and the solid at 120*s*.; the chemically pure acetate costs 8*s*. per kilo.

STANNOUS ACETATE, $Sn(C_2H_3O_2)_2$, is obtained by treating stannous chloride with lead acetate or by dissolving freshly precipitated stannous hydroxide in dilute acetic acid. Its solution is used as a mordant or corrosive in printing cotton with substantive dyes (*see this*, Part III).

The 20° to 22° Bé. solution costs 48*s*. per quintal.

NORMAL CUPRIC ACETATE (Crystallised Verdigris), $Cu(C_2H_3O_2)_2 + H_2O$, is obtained by dissolving the basic acetate (true verdigris) in acetic acid or, better, by decomposing copper sulphate solution with lead acetate. It forms clinorhombic, dark green prisms and is readily soluble in hot water (1 : 5) or in alcohol. It is used in medicine and has been suggested as a means of combating the *Peronospora*, which attacks the vine. It costs 2*s*. 6*d*. per kilo.

BASIC COPPER ACETATE (Verdigris), $[2Cu(C_2H_3O_2)OH] + 5H_2O$, is obtained by arranging sheets of copper with flannel saturated with hot vinegar, acetic acid, or acid vinasse, in between. The crust of acetate is detached from the plates and sold in cakes either dry or with 30 per cent. of moisture. It forms blue needles or scales, which effloresce in the air and become green, owing to loss of water.

It dissolves only slightly in water and, when heated in the dry state, gives off acetic acid and water. When pure, it is completely soluble in excess of ammonium carbonate solution.

It was formerly used as a colouring-matter, but is now used for the preparation of *Schweinfurth's green* (*copper aceto-arsenite*), $Cu(C_2H_3O_2)_2$, $3CuAs_2O_4$, by mixing with the requisite proportion of arsenious anhydride solution; this gives a beautiful green colouring-matter, which is still used to some extent, although it is very poisonous owing to the evolution of hydrogen arsenide in the air.

In cakes or balls, the basic acetate costs £6 per quintal, whilst the refined powder costs £8 10*s*.

[1] *Analysis of lead acetate* is effected by dissolving 5 grms. of it in water, precipitating the lead with a known quantity, in slight excess, of normal sulphuric acid, making up to 250 c c and then adding a volume of water about equal to that of the precipitate. In 50 c c. of the filtrate, the sulphuric acid is precipitated with barium chloride, the weight of the resulting barium sulphate giving the quantity of sulphuric acid which has remained in combination with the lead Another 50 c c. of the filtrate is titrated with normal caustic potash, the total acidity thus found being due to acetic acid and excess of sulphuric acid; deduction of the latter then gives the amount of acetic acid existing in combination in the lead acetate

PROPIONIC ACID, $C_3H_6O_2$ or $CH_3 \cdot CH_2 \cdot COOH$

This acid is obtained by hydrolysing ethyl cyanide (*see* p. 199) and also by the action of certain micro-organisms on calcium lactate. It is, however, usually prepared by fermenting wheat-bran, or is extracted from crude pyroligneous acid, being formed in small quantity in the dry distillation of wood ; it can also be easily obtained by oxidising normal propyl alcohol with chromic anhydride. For some years it has been manufactured by the Effront process (*see* p. 155) from the residues of beetroot *molasses :* 1000 kilos of molasses yield 75 kilos of ammonium sulphate and 95 to 120 of fatty acids consisting largely of propionic acid (*see also* section on Sugar).

It is a liquid of sp. gr. 0·992 and resembles acetic acid in odour and in physical and chemical properties. It boils at 141° and solidifies at −22°. It forms crystalline salts soluble in water, and its esters have a fruity aroma. Chemically pure propionic acid costs 32*s.* per kilo, and the commercial acid formerly cost 14*s.* 6*d.*, but nowadays the Effront process yields a much cheaper commercial acid, which in practice may be used to replace formic and acetic acids, these being more difficult to purify.

BUTYRIC ACIDS, $C_4H_8O_2$

Two isomerides are known of different structures, their constitutional formulæ being deduced from their methods of synthesis.

(1) NORMAL BUTYRIC ACID (Butanoic or Propylcarboxylic Acid or Butyric Acid of Fermentation), $CH_3 \cdot CH_2 \cdot CH_2 \cdot COOH$, is the more important of the two isomerides and exists in butter in the form of glyceric ester to the extent of 4 to 5 per cent. It is formed also in sweat and occurs in solid excreta and in decomposing cheese, as well as among products of fermentation of glycerine.

It is obtained, not by synthesis (*see* p. 265), but by the butyric fermentation of starch-paste in presence of a little tartaric acid, putrefied meat or cheese being added after a few days (pure cultures of special bacteria are also used at the present time) ; it is also obtained from acid skim milk by treatment with powdered marble and converting the calcium lactate into calcium butyrate, then into the sodium salt, and finally, by means of H_2SO_4, into the free acid. It is also obtained from molasses residues by Effront's process (*see above*).

It forms an oily liquid, sp. gr. 0·958 at 14°, boiling at 162° and solidifying in scales at 19°. It dissolves in water, alcohol, or ether, burns with a bluish flame, and gives crystalline, slightly soluble salts.

Calcium Butyrate, $(C_4H_7O_2)_2Ca + H_2O$, is less soluble in hot than in cold water.

The esters have pleasant, fruity odours, and are used to produce artificial rum. Commercial concentrated butyric acid costs 4*s.* per kilo ; the 50 per cent. acid 2*s.* 6*d.* ; and the chemically pure (100 per cent.) 5*s.* 10*d.* The concentrated esters are sold at 2*s.* 6*d.* to 5*s.* per kilo.

(2) ISOBUTYRIC ACID (2-Methylpropanoic or Dimethylacetic Acid), $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!>\!CH \cdot COOH$, resembles the preceding acid, but is less soluble in water. It boils at 154° and solidifies at −79°, and occurs free in arnica and carob roots and as ester in chamomile oil. It can be obtained by the ordinary synthetic processes and is less resistant than the normal acid to oxidising agents. The pure acid costs 40*s.* per kilo and the commercial acid about one-half as much.

The **Calcium Salt**, $Ca(C_4H_7O_2)_2$, is more soluble in hot water than in cold.

VALERIC ACIDS, $C_5H_{10}O_2$

The four isomerides predicted by theory are known.

(1) NORMAL VALERIC ACID (Pentanoic or Propylacetic Acid), $CH_3 \cdot [CH_2]_3 \cdot COOH$, is a dense liquid (sp. gr. 0·956 at 0°), boiling at 185° and solidifying at −58·5°. It is obtained synthetically from propylmalonic acid or butyl cyanide and is met with in

pyroligneous acid; it is slightly soluble in water. The pure product costs *5d.* per gramme.

(2) ISOVALERIC ACID, $\frac{CH_3}{CH_3}>CH\ CH_2 \cdot COOH$, is found free or in the form of esters in animals (fat of the dolphin, sweat of the feet, &c.) and vegetables (roots of *Valeriana officinalis*), and from the latter can be extracted by boiling with solutions of soda or by distilling with water containing phosphoric acid. It is a liquid (sp. gr. 0·947 at 0°), boiling at 174° and solidifying at −15°; it has a disagreeable odour of stale cheese. It is often obtained by oxidising fusel oil with dichromate and sulphuric acid. The pure acid costs 96*s.* per kilo.

Its esters are used as *artificial fruit essences* and cost from 10*s.* to 16*s.* per kilo.

(3) ETHYLMETHYLACETIC ACID (Methyl-2-butanoic or Active Valeric Acid), $\frac{CH_3}{C_2H_5}>CH \cdot COOH$, is optically active as it contains an asymmetric carbon atom (*see* p. 18); it occurs naturally with isovaleric acid. The inactive mixture of the two oppositely active acids can be resolved into its active components by means of the brucine salts. It boils at 174°.

(4) TRIMETHYLACETIC ACID (Dimethyl-2-propanoic or Pivalic Acid), $(CH_3)_3 \vdots C \cdot COOH$, is a solid, m.pt. 35°, b.pt. 163°. It has an odour resembling that of acetic acid, and it can be obtained from tertiary butyl cyanide.

HIGHER ACIDS

Of the numerous isomerides theoretically possible and of the many actually known, mention will be made only of some of the more important which occur naturally and are usually of the normal structure and with even numbers of carbon atoms.

NORMAL CAPROIC ACID, $C_6H_{12}O_2$ or $CH_3 \cdot [CH_2]_4 \cdot COOH$, is a liquid boiling at 205° and solidifying at −1·5°. It is volatile in steam, has an unpleasant odour like rancid butter, and is found free in Limburger cheese and coco-nut oil, and as glyceride in goats' butter. It is formed on oxidising proteins or higher fatty acids (unsaturated).

HEPTOIC ACID (Œnantic Acid), $C_7H_{14}O_2$ or $CH_3 \cdot [CH_2]_5 \cdot COOH$, is formed on oxidation of castor oil or *œnanthaldehyde*. It is a liquid boiling at 220° and solidifying at −20°. It differs from its lower homologues by exhibiting a slight odour of fat.

CAPRYLIC ACID (Octoic Acid), $C_8H_{16}O_2$ or $CH_3 \cdot [CH_2]_6 \cdot COOH$, solidifies at 16·5° and boils at 237·5°; it is found in coco-nut oil and as glyceride in ordinary butter and that of goats.

NONOIC ACID (Pelargonic Acid), $C_9H_{18}O_2$ or $CH_3 \cdot [CH_2]_7 \cdot COOH$, is a liquid boiling at 254°. It is formed by oxidising oleic acid or by decomposing the *ozonide of oleic acid* (Molinari and Soncini, 1905) with dilute alkali. In nature it occurs in *Pelargonium roseum*.

DECOIC ACID (Capric Acid), $C_{10}H_{20}O_2$ or $CH_3 \cdot [CH_2]_8 \cdot COOH$, is a solid, melting at 31·4° and boiling at 200° under 100 mm. pressure. It also is found in coco-nut oil and goats' butter.

UNDECOIC ACID, $C_{11}H_{22}O_2$ or $CH_3 \cdot [CH_2]_9 \cdot COOH$. Distillation of castor oil under reduced pressure yields the unsaturated *undecenoic acid*, $C_{11}H_{20}O_2$, which gives undecoic acid on reduction with hydrogen. It melts at 28° and boils at 212° (100 mm.).

LAURIC ACID, $C_{12}H_{24}O_2$ or $CH_3 \cdot [CH_2]_{10} \cdot COOH$, is a solid, melting at 44° and boiling at 225° (100 mm.); it occurs in the form of glyceride in laurel berries.

MYRISTIC ACID, $C_{14}H_{28}O_2$ or $CH_3 \cdot [CH_2]_{12} \cdot COOH$, melts at 54° and boils at 248° (100 mm.). It is found as glyceride (*myristin*) in the nutmeg (*Myristica moschata*) and in ox-gall, and abounds in the seeds of *Virola Venezuelensis*.

PALMITIC ACID (Hexadecoic Acid), $C_{16}H_{32}O_2$ or $CH_3 \cdot [CH_2]_{14} \cdot COOH$, forms a moderately transparent white mass, which readily softens and melts at 62·6°. It is insoluble in water and crystallises from alcohol in scales or needles. It boils unchanged at 268° under 100 mm. pressure, or, with partial decomposition, at 339° to 356° under the ordinary pressure.

It is one of the normal components of animal and vegetable fats, in which it occurs as a glyceride (palmitin), and is easily obtained, together with oleic acid, from palm oil by hydrolysing and then decomposing the soap formed, the palmitic acid is then isolated by fractional crystallisation. *Japanese vegetable wax* consists almost exclusively of palmitin. The industrial treatment of fats and oils for the extraction of the corresponding fatty acids (palmitic, stearic, and oleic) will be described in the section dealing with the manufacture of soap and candles.

Commercial palmitic acid is also known by the inaccurate name of *palmitin* and is likewise manufactured by melting oleic acid with potassium hydroxide (*Varrentrapp's reaction*): $C_{18}H_{34}O_2 + 2KOH = H_2 + CH_3 \cdot CO_2K + C_{16}H_{31}O_2K$ (potassium palmitate, which gives palmitic acid under the action of mineral acid).

Its alkali salts (*soaps*) are soluble in alcohol or water, but considerable dilution of the aqueous solutions results in the separation of an acid salt and liberation of alkali. Whilst in alcoholic solution these soaps show virtually normal molecular weights, the aqueous solutions show no rise in the boiling-point, the soaps thus behaving as colloids in these solutions (*see* vol. i, p. 102). The other salts (*palmitates*) are insoluble in water and, in some cases, soluble in alcohol; mineral acids liberate palmitic acid from them.

The commercial acid costs £4 per quintal, the refined product £8, and the doubly refined 25*s*. 6*d*. per kilo.

MARGARIC ACID, $C_{17}H_{34}O_2$ or $CH_3 \cdot [CH_2]_{15} \cdot COOH$, was for a long time thought to exist in fats, but it has been shown that a mixture of palmitic (C_{18}) and stearic (C_{16}) acids was being dealt with. Synthetically it can be obtained by hydrolysing cetyl cyanide, $C_{16}H_{33} \cdot CN$, and by other methods. It melts at 60° and distils unchanged at 277° under 100 mm. pressure.

STEARIC ACID, $C_{18}H_{36}O_2$ or $CH_3 \cdot [CH_2]_{16} \cdot COOH$, which is improperly known commercially as *stearine* (and is then mixed with palmitic acid), and its separation from oleic acid will be described when dealing with candles.

As glyceride, it occurs with that of oleic acid as one of the principal constituents of fats and oils, and is usually prepared industrially from beef suet.

Synthetically it can be obtained by the reducing action of hydrogen on oleic acid (*see this*), and the constitution of the latter being known, that of stearic acid follows directly. Industrial application is now made of this process, the catalytic reaction of Sabatier and Senderens being employed.

It forms a somewhat soft white mass, melting at 69·3°, and crystallises from alcohol in shining scales. It boils unchanged at 287° under 100 mm. pressure or with partial decomposition at 359° to 383° under the ordinary pressure.

It is insoluble in water, soluble slightly in light petroleum, and more readily in alcohol, ether, benzene, or carbon disulphide.

Its salts behave like those of palmitic acid. The lead salts of these high fatty acids are obtained by boiling the fats or oils with lead oxide and water. This *lead soap* is used for the preparation of *lead plaster*, and is used in the manufacture of varnish. Stearic acid made into a paste with gypsum forms a kind of *artificial ivory*.

Italy imported, especially from France, England, and Belgium, 17,080 quintals of stearic acid in 1906; 12,500 in 1908; and 14,450 (of the value of £63,570) in 1910.

CEROTIC or **CEROTINIC ACID**, $C_{27}H_{54}O_2$, is found free in beeswax (together with **Melissic Acid**, $C_{30}H_{60}O_2$), as ester in Chinese wax and as glyceride in the fat of raw wool. It melts at 78·5° and is converted by oxidising agents into various acids with lower molecular weights.

II. UNSATURATED MONOBASIC FATTY ACIDS

A. OLEIC or ACRYLIC SERIES, $C_nH_{2n-2}O_2$ (Olefine-Carboxylic Acids)

Empirical formula	Name of acid		Constitutional formula	Melting-point	Boiling-point
$C_3H_4O_2$	Acrylic acid		$CH_2:CH\cdot CO_2H$	13°	140°
$C_4H_6O_2$	Crotonic	Vinylacetic acid	$CH_2:CH\cdot CH_2\cdot CO_2H$	−39°	163°
		Solid crotonic acid	$CH_3\cdot CH:CH\cdot CO_2H$ (*cis*)	72°	181°
		Liquid crotonic acid	$CH_3\cdot CH:CH\cdot CO_2H$ (*trans*)	15.5°	169°
		Metacrylic acid	$CH_2:C(CH_3)\cdot CO_2H$	16°	161°
$C_5H_8O_2$	(8 structural isomerides and one stereoisomeride)	Angelic acid	$CH_3—C—CO_2H$ $\Vert$ $CH_3—C—H$	45°	185°
		Tiglic acid	$CH_3\cdot C—CO_2H$ $\Vert$ $H—C—CH_3$	65°	198.5°
$C_6H_{10}O_2$	(Not all stereoisomerides known)	Pyroterebic acid	$(CH_3)_2 . C:CH\cdot CH_2\cdot CO_2H$	−15°	207°
$C_7H_{12}O_2$	Do.	γ-Allylbutyric acid	$CH_2:CH\cdot[CH_2]_3\cdot CO_2H$	—	226°
$C_7H_{12}O_2$	Do.	Teracrylic acid	$(CH_3)_2:C:C(CH_3)\cdot CH_2\cdot CO_2H$	—	218°
$C_{10}H_{18}O_2$	Do.	Citronellic acid	$CH_2:C(CH_3)\cdot[CH_2]_3\cdot CH(CH_3)\cdot CH_2\cdot CO_2H$	—	152° (18 mm.)
$C_{11}H_{20}O_2$	Do.	Undecenoic acid	$CH_2:CH\cdot[CH_2]_8\cdot CO_2H$	24.5°	213.5° (100 mm.)
$C_{16}H_{30}O_2$	Do.	Hypogæic acid	$CH_3\cdot[CH_2]_7\cdot CH:CH\cdot[CH_2]_5\cdot CO_2H$	—	—
$C_{18}H_{34}O_2$	Do.	Oleic acid	$CH_3\cdot[CH_2]_7\cdot CH:CH\cdot[CH_2]_7\cdot CO_2H$ (*cis*)	14°	223° (10 mm.)
		Elaidic acid	$CH_3\cdot[CH_2]_7\cdot CH:CH\cdot[CH_2]_7\cdot CO_2H$ (*trans*)	51°	225° (10 mm.)
$C_{18}H_{34}O_2$	Do.	Iso-oleic acid	$CH_3\cdot[CH_2]_8\cdot CH:CH\cdot[CH_2]_6\cdot CO_2H$ (?)	44°	—
		$\Delta\alpha\beta$-oleic acid	$CH_3\cdot[CH_2]_{14}\cdot CH:CH\cdot CO_2H$	58°	—
$C_{22}H_{42}O_2$	Do.	Erucic acid	$CH_3\cdot[CH_2]_7\cdot CH:CH\cdot[CH_2]_{11}\cdot CO_2H$	34°	254.5° (10 mm.)
		Brassidic acid	$CH_3\cdot[CH_2]_7\cdot CH:CH\cdot[CH_2]_{11}\cdot CO_2H$	65°	256° (10 mm.)
		Isoerucic acid	$CH_3\cdot[CH_2]_8\cdot CH:CH\cdot[CH_2]_{10}\cdot CO_2H$ (?)	55°	—

Their importance is due to the fact that certain of them occur as glycerides in many fats and oils.

GENERAL PROCESSES OF FORMATION. The following are the most important of these:

(1) The unsaturated halogen derivatives of unsaturated alcohols can be transformed into cyanogen derivatives, which give the corresponding acids on hydrolysis (*see* p. 199):

$$CH_2:CH\cdot CH_2\cdot OH \longrightarrow CH_2:CH\cdot CH_2\cdot Br \longrightarrow$$
$$CH_2:CH\cdot CH_2\cdot CN \longrightarrow CH_2:CH\cdot CH_2\cdot COOH.$$

(2) Oxidation of unsaturated alcohols and aldehydes with mild oxidising agents (silver oxide or the oxygen of the air) which do not attack the double linking; allyl alcohol and acrolein give acrylic acid.

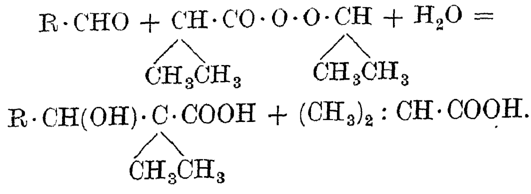
(3) Of general use is *Perkin's reaction* applicable especially to the aromatic series, but of service also for the fatty series: when an aldehyde is heated with the sodium salt of a saturated fatty acid in presence of an anhydride (*e.g.* acetic anhydride) and then treated with water, the resulting products are the saturated acid corresponding with the aldehyde used and an unsaturated acid, which always has the double linking between the α- and β-carbon atoms, the α-carbon atom being that adjacent to the carbonyl group, CO. If the chain united to the aldehyde group is denoted by R, the intermediate phases of this reaction are probably as follow:

(*a*) $R\cdot CHO + CH_3\cdot CO\cdot O\cdot CO\cdot CH_3$ give, by aldol condensation, $R\cdot CH(OH)\cdot CH_2\cdot CO\cdot O\cdot CO\cdot CH_3$; this unstable compound immediately

separates water, giving $R\cdot CH:CH\cdot CO\cdot O\cdot CO\cdot CH_3$, treatment of this product with water yielding the unsaturated acid:

$$(b)\quad R\cdot CH:CH\cdot CO\cdot O\cdot CO\cdot CH_3+H_2O = CH_3\cdot COOH+R\cdot CH:CH\cdot COOH.$$

It is evident that, if only one hydrogen atom is united to the carbon atom adjacent to the carbonyl group of the original anhydride, the first phase of the reaction, but not the second, will be possible, so that only a saturated hydroxy-acid will be obtained:



The presence of the sodium salt of the fatty acid is indispensable to all these reactions, but its function has not yet been explained.

(4) Similar to *Perkin's synthesis* is the reaction between an aldehyde (or an α-ketonic acid, $R\cdot CO\cdot COOH$, which possibly loses CO_2 and thus gives an aldehyde) and malonic acid in presence of glacial acetic acid, a mixture of unsaturated monobasic acids with the double linking in the $\alpha\beta$- or $\beta\gamma$-position being obtained and CO_2 split off:

$$(a)\quad R\cdot CH_2\cdot CHO + \underset{\text{Malonic acid}}{CH_2{<}^{COOH}_{COOH}} = R\cdot CH_2\cdot CH(OH)\cdot CH{<}^{COOH}_{COOH}$$

$$(b)\qquad 2R\cdot CH_2\cdot CH(OH)\cdot CH{<}^{COOH}_{COOH} =$$

$$2CO_2 + 2H_2O + \underset{\alpha\beta\text{-acid}}{R\cdot CH_2\cdot CH:CH\cdot COOH} + \underset{\beta\gamma\text{-acid}}{R\cdot CH:CH\cdot CH_2\cdot COOH}.$$

It should be noted that this reaction always gives also a condensation product of 1 mol. of the aldehyde and 2 mols. of malonic acid, this product then losing CO_2 and yielding a saturated dibasic acid:

$$R\cdot CH{<}^{CH(COOH)_2}_{CH(COOH)_2} = 2CO_2 + R\cdot CH{<}^{CH_2\cdot COOH}_{CH_2\cdot COOH}$$

(5) When monohalogenated saturated fatty acids (especially those with the halogen in the β-position) are heated with alcoholic potash or sometimes even with water alone, a molecule of halogen hydracid is eliminated and the unsaturated acid formed (similar to the reaction giving unsaturated hydrocarbons, p. 88):

$$\underset{\beta\text{-Iodopropionic acid}}{CH_2I\cdot CH_2\cdot COOH} = HI + \underset{\text{Acrylic acid}}{CH_2:CH\cdot COOH.}$$

(6) By separating a molecule of water from monohydroxy-acids by means of distillation or a dehydrating agent (H_2SO_4, PCl_5, P_2O_5) or sometimes by merely heating with caustic soda solution, the unsaturated monobasic fatty acids are formed:

$$\underset{\beta\text{-Hydroxybutyric acid}}{CH_3\cdot CH(OH)\cdot CH_2\cdot COOH} = H_2O + \underset{\text{Crotonic acid}}{CH_3\cdot CH:CH\cdot COOH.}$$

GENERAL PROPERTIES. The number of double bonds is ascertained by the same methods as are applied to unsaturated hydrocarbons (*see* pp. 88 and 89)—by addition of either halogen or ozone. These unsaturated acids are more energetic than the corresponding saturated acids with the same

numbers of carbon atoms, as can be seen from their ionisation constants (vol. i, p. 92). They are more easily oxidisable than the saturated acids, powerful oxidising agents rupturing the carbon atom chain at the double linking, the position of which can hence be established by a study of the compositions of the two acids formed.

When boiled with 10 per cent. caustic soda solution, unsaturated acids with a double linking (Δ) in the $\beta\gamma$-position undergo displacement of this linking with the *partial* formation of unsaturated acids with a double bond in the $\alpha\beta$-position (Fittig, 1891–1894); this is formed from an intermediate hydroxy-acid, an equilibrium being established as indicated below:

$$\underset{\beta\gamma\text{-acid}}{R\cdot CH:CH\cdot CH_2\cdot COOH} + H_2O \rightleftarrows \underset{\beta\text{-Hydroxy-acid}}{R\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot COOH} \rightleftarrows$$
$$H_2O + \underset{\alpha\beta\text{-acid}}{R\cdot CH_2\cdot CH:CH\cdot COOH}.$$

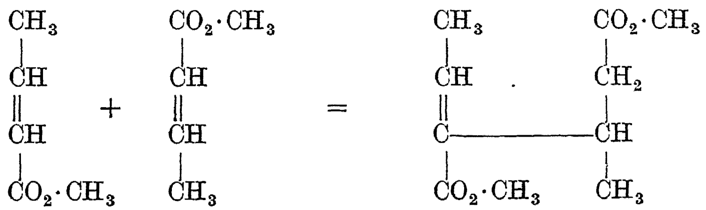
In general this reaction preponderates towards the formation of the $\alpha\beta$-acid and not *vice versa*, the carboxyl group apparently exerting an attraction on the double linking.

When an unsaturated acid is fused with caustic soda or potash, the double linking is displaced, giving an $\alpha\beta$-acid, the new molecule immediately splitting at the double bond, the resultant products being acetic acid and another saturated acid. This displacement of the double linking was unknown until a few years ago, so that oleic acid, for example, which gives palmitic and acetic acids quantitatively when fused with potash, was regarded as an $\alpha\beta$-unsaturated acid. It has, however, been shown (*see later*) that the double bond of oleic acid is in the middle of the molecule, the action of the potash causing displacement of this bond before the molecule is resolved:

$$\underset{\text{Oleic acid}}{CH_3\cdot[CH_2]_7\cdot CH:CH\cdot[CH_2]_7\cdot COOH} \longrightarrow \underset{\alpha\beta\text{-Oleic acid}}{CH_3\cdot[CH_2]_{14}\cdot CH:CH\cdot COOH}$$

$$CH_3\cdot[CH_2]_{14}\cdot CH:CH\cdot COOH + 2KOH + O =$$
$$\underset{\text{Potassium palmitate}}{CH_3\cdot[CH_2]_{14}\cdot COOK} + H_2O + CH_3\cdot COOK.$$

The acids of the oleic and acrylic series, and unsaturated compounds in general, exhibit a tendency to *polymerise;* the mere action of sodium alkoxide on the crotonic esters produces, in addition to other reactions, the following change:



Methyl crotonate Methyl dicrotonate

Instances of *stereoisomerism* among unsaturated compounds have already been described on pp. 16 and 17, and it is only necessary to state here that, of the two stereoisomerides corresponding with one and the same formula, one is less stable than the other, into which it is easily and directly transformed (the inverse change only takes place indirectly) by mere heating or by the action of concentrated sulphuric acid, caustic soda, a little nitrous acid, or a trace of bromine in the presence of light.

ACRYLIC ACID (Propenoic Acid)

$C_3H_4O_2$ or $CH_2 : CH\ COOH$

This acid was prepared for the first time (Redtenbacher, 1843) by oxidising acrolein $CH_2 : CH\cdot CHO$, with silver oxide. It is now more readily obtained indirectly, by the action of gaseous hydrogen chloride, which gives β-chloropropaldehyde, $CH_2Cl\cdot CH_2\ CHO$, this being converted by nitric acid into the corresponding β-chloropropionic acid, $CH_2Cl\cdot CH_2\cdot COOH$; when the last compound is boiled with a solution of alkali, it loses HCl, yielding acrylic acid.

Another convenient synthesis is the following: allyl alcohol (a, *see below*) with bromine gives dibromopropyl alcohol (b), which, on oxidation, yields $\alpha\beta$-dibromopropionic acid (c), and this, by the action of either zinc in presence of dilute sulphuric acid (or water) or reduced copper (containing iron) loses bromine and gives acrylic acid (d):

$$\begin{array}{ccccccc} CH_2 & & CH_2Br & & CH_2Br & & CH_2 \\ \| & & | & & | & & \| \\ CH & \longrightarrow & CHBr & \longrightarrow & CHBr & \longrightarrow & CH \\ | & & | & & | & & | \\ CH_2\cdot OH & & CH_2\ OH & & COOH & & COOH \\ \text{a} & & \text{b} & & \text{c} & & \text{d} \end{array}$$

Acrylic acid is a liquid soluble in water and having a pungent odour almost like that of acetic acid: it has the sp. gr. 1·0621 at 16°, boils and polymerises at about 140°, and when cooled forms tabular crystals melting at 13°. With nascent hydrogen, it is transformed into propionic acid, whilst, when fused with potash, it gives acetic and formic acids.

CROTONIC ACIDS, $C_4H_6O_2$

Isomeric unsaturated acids of this formula are possible theoretically—two stereoisomerides and the others structural isomerides. The following acids have actually been prepared:

(*a*) $CH_2 : CH\cdot CH_2\cdot COOH$, *vinylacetic acid;*

(*ba*) $\begin{array}{c} H—C—CO_2H \\ \| \\ H—C—CH_3 \end{array}$, *cis* β-methylacrylic acid (*solid crotonic acid*);

(*bβ*) $\begin{array}{c} H—C—CO_2H \\ \| \\ CH_3—C—H \end{array}$, *trans* β-methylacrylic acid (*liquid crotonic acid*);

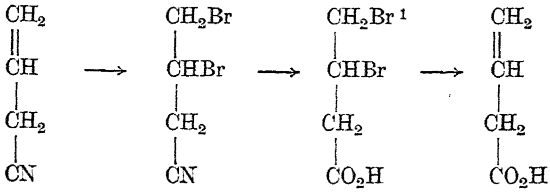
(*c*) $CH_2 : C\!<\!\begin{array}{l} CH_3 \\ COOH \end{array}$, methylmethyleneacetic or α-methylacrylic acid.

With the general formula, $C_4H_6O_2$, there corresponds also ethylene-acetic or trimethylenecarboxylic acid, $\begin{array}{c} CH_2 \\ | \\ CH_2 \end{array}\!\!>\!CH\cdot COOH$, but this does not belong to the olefinecarboxylic acids as it contains no double linking, and it will therefore be studied with the cyclic compounds.

(*a*) **VINYLACETIC ACID, $CH_2 : CH\cdot CH_2\ CO_2H$,** has been prepared, only recently, by distilling β-hydroxglutaric acid in a vacuum:

$$\begin{array}{ccc} CH_2\cdot CO_2H & & CH_2 \\ | & & \| \\ CH\cdot OH & = \quad CO_2 + H_2O + & CH \\ | & & | \\ CH_2\cdot CO_2H & & CH_2\cdot CO_2H \end{array}$$

and also by first brominating (with bromine dissolved in CS_2) allyl cyanide, hydrolysing the product, and finally removing the bromine by means of zinc dust and alcohol, thus:



Vinylacetic acid is a very hygroscopic liquid, which solidifies when cooled to a low temperature ; it melts at $-39°$ and boils at $163°$. Its calcium salt, $(C_4H_5O_2)_2Ca, H_2O$, crystallises from water in shining needles.

When boiled with 5 per cent. sulphuric acid solution, it is transformed into the solid crotonic acid, $CH_2 : CH \cdot CH_2 \cdot COOH \longrightarrow CH_3 \cdot CH : CH \cdot COOH$.

This transposition of the double linking is also effected by boiling with caustic soda solution, but in this case a preponderance of β-hydroxybutyric acid is formed at the same time.

($b\alpha$) **ORDINARY** or **SOLID CROTONIC ACID**, $\begin{array}{c} H—C—CO_2H \\ \| \\ H—C—CH_3 \end{array}$ (cis β-*methylacrylic acid* or cis *ethylideneacetic acid ;* also wrongly known as α-*crotonic acid*). Its constitution follows from its synthesis from α-bromobutyric acid (or rather its ester) by the elimination of HBr under the action of alcoholic potash :

$$CH_3 \cdot CH_2 \cdot CHBr \cdot CO_2H = HBr + CH_3 \cdot CH : CH \cdot CO_2H.$$

From water (solubility 1 in 12) the acid crystallises in shining needles melting at 71° to 72° ; it boils at 181° to 182°, has an odour resembling that of butyric acid, and is found free in crude pyroligneous acid. Its calcium and barium salts contain no water of crystallisation and are very soluble in water.

When gently oxidised in alkaline solution with permanganate, it gives $\alpha\beta$-*dihydroxybutyric acid*, $CH_3 \cdot CH(OH) \cdot CH(OH) \cdot CO_2H$, which cannot form a *lactone*, so that neither of its hydroxyl groups is in the γ-position ; the double linking of the crotonic acid must hence be between the α- and β-carbon atoms. When halogen hydracids are added to it, the halogen goes to the β-position. With nascent hydrogen it gives butyric acid.

($b\beta$) **LIQUID CROTONIC ACID**, $\begin{array}{c} H—C—CO_2H \\ \| \\ CH_3—C—H \end{array}$ (trans β-*methylacrylic acid* or *isocrotonic* or *allocrotonic acid ;* known improperly as β-crotonic acid). This acid is prepared from ethyl acetoacetate, which, with PCl_5, gives probably a chloracetic ester, the latter losing a molecule of HCl and yielding the two stereoisomeric chloroisocrotonic acids (or the corresponding ethyl esters) ; these two isomerides can be separated, the one formed in greater proportion being readily, and the other difficultly, distilled in steam. The latter gives solid, and the other liquid, crotonic acid on reduction with sodium amalgam :

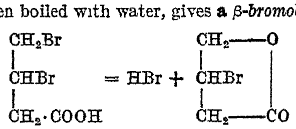
$$(a) \quad \underset{\text{Ethyl acetoacetate}}{CH_3 \cdot CO \cdot CH_2 \cdot CO \cdot OC_2H_5} + PCl_5 = \underset{\text{Intermediate product}}{CH_3 \cdot CCl_2 \cdot CH_2 \cdot CO \cdot OC_2H_5} + POCl_3.$$

$$(b) \quad CH_3 \cdot CCl_2 \cdot CH_2 \cdot CO \cdot OC_2H_5 = \underset{\text{Two stereoisomerides}}{CH_3 \cdot CCl : CH \cdot CO \cdot OC_2H_5} + HCl.$$

$$(c) \quad CH_3 \cdot CCl : CH \cdot CO \cdot OC_2H_5 + H_2 = \underset{\text{Ethyl ester of crotonic acid}}{CH_3 \cdot CH : CH \cdot CO \cdot OC_2H_5} + HCl.$$

The isocrotonic acid thus obtained is liquid, but is not pure, as it always contains ordinary crotonic acid and a little *tetrolic acid*, $CH_3 \cdot C \vdots C \cdot CO_2H$. Only within recent

[1] This $\beta\gamma$-*dibromobutyric acid*, when boiled with water, gives a β-*bromobutyrolactone :*



Lactones are not usually formed by acids brominated in the α- or β-position, but only with those where the bromine atom is in the γ-position. It may hence be concluded that the double linking in vinylacetic acid is also in the $\beta\gamma$-position, since its brominated derivative gives a lactone, which is formed only when there is halogen in the γ-position.

years (1895 and 1904) has it been separated from these admixtures, either by means of its sodium salt, which is more soluble in alcohol, or by means of its quinine salt, which is less soluble in water than that of crotonic acid.

After such purification it is found that pure liquid crotonic acid forms crystals melting at 15·5° and boiling at 169° under the ordinary pressure or at 74° under a pressure of 15 mm. The calcium salt, $(C_4H_5O_2)_2Ca, 3H_2O$, forms large prisms, and the barium salt, $(C_4H_5O_2)_2Ba, H_2O$, large plates.

When heated above 100°, it is converted partially into normal crotonic acid, and in order to avoid this change during distillation the operation is carried out in a vacuum ; the transformation is instantaneous and quantitative in presence of a trace of bromine in aqueous solution or of carbon disulphide under the influence of direct sunlight.

That the structure of isocrotonic acid is the same as that of crotonic acid and not of vinylacetic acid is supported by the fact that isocrotonic acid gives no lactonic derivative (*see above*) and also by the fact that the *peroxyozonides* of these two acids, obtained by Harries and Langheld (1905) by the action of ozonised oxygen and having the structure

$$\begin{array}{l} CH_3\cdot \underset{|}{C}H—\underset{|}{C}H\cdot C\!\begin{matrix}\diagup OH \\ \diagdown O:O\end{matrix} \\ \quad\; O\cdot O\cdot O \end{array}$$

, give with water the same decomposition products, namely, hydrogen peroxide, acetaldehyde, and glyoxylic acid, $CHO\cdot CO_2H$.

(*c*) METHYLMETHYLENEACETIC ACID (*α*-Methylacrylic, Metacrylic or Methylpropenoic Acid), $CH_2:C\!\begin{matrix}\diagup CH_3 \\ \diagdown CO_2H\end{matrix}$, can be obtained by separation of water from *α*-hydroxyisobutyric acid and also by elimination of a molecule of HBr from *α*-bromoisobutyric acid :

$$\begin{array}{c} CH_3\cdot \underset{\displaystyle\overset{|}{CH_3}}{C}\cdot Br\cdot CO_2H = HBr + CH_2:C\!\begin{matrix}\diagup CH_3 \\ \diagdown CO_2H\end{matrix} \end{array}$$

This synthesis indicates the constitution of metacrylic acid, which is confirmed by the observation that reduction of this acid by means of sodium amalgam gives isobutyric acid, this having a known constitution.

Metacrylic acid crystallises readily from water in shining prisms which melt at + 16° and boil at 161°, or at 60° to 63° under 12 mm. pressure. It has a strong but not unpleasant odour of bad mushrooms and occurs in Roman chamomile ; it dissolves very readily in alcohol or ether. It exhibits a marked tendency to polymerise, more especially at 130°, but also in the cold when in contact with concentrated hydrochloric acid. The calcium salt forms crystals very soluble in water.

PENTENOIC ACIDS, $C_5H_8O_2$

Several isomeric pentenoic acids are known, those which have been most closely studied being :

(*a*) ANGELIC ACID (*α*-Ethylidenepropionic, *αβ*-Dimethylacrylic or 2-Methyl-2-butenoic-1 Acid), $\begin{array}{l} CH_3—C—CO_2H \\ \qquad\;\, \| \\ CH_3—C—H \end{array}$. The double linking in this acid must be in the *αβ*-position, since lactonic derivatives are unknown. On protracted heating it is transformed into the stereoisomeric *tiglic acid.*

Angelic acid was first found in, and is still obtained from, the roots of *Angelica arcangelica,* and as ether in Roman chamomile oil. The pure crystals melt at 45°, boil at 185°, and are only slightly soluble in water or volatile in steam.

(*b*) TIGLIC ACID, $\begin{array}{l} CH_3—C—CO_2H \\ \qquad\;\, \| \\ \;\;H—C—CH_3 \end{array}$, often occurs with angelic acid and is formed in the decomposition of various more complex organic compounds. It can be prepared synthetically from acetaldehyde and ethyl *α*-bromopropionate in presence of zinc, a ydroxy-acid being formed as an intermediate compound. It forms transparent crystals, m.p. 65°, b.pt. 198·5°, and is slightly soluble in cold and readily in hot water ; it has a pleasant smell and is volatile in steam.

PYROTEREBIC ACID (2-Methyl-2-pentenoic-5 Acid), $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C:CH\cdot CH_2\cdot COOH$, is formed by the distillation of an oxidation product (*terebic acid*) of oil of turpentine (together with the lactone of isocaproic acid, *see below*).

$$\begin{array}{l}(CH_3)_2\cdot C\cdot CH(CO_2H)\cdot CH_2\\ \quad\;|\qquad\qquad\qquad\quad |\\ \quad O\text{———————}CO\end{array} \;=\; CO_2 + (CH_3)_2:C:CH\cdot CH_2\cdot COOH.$$

Terebic ($\gamma\gamma$-dimethylparaconic) acid — Pyroterebic acid

That pyroterebic acid really has this constitution is shown by the fact that, on reduction with hydriodic acid, it gives isocaproic acid of the known constitution $(CH_3)_2\cdot CH\cdot CH_2\cdot CH_2\cdot COOH$. The position of the double linking is confirmed by the great ease with which it is converted into *isocaproic lactone* on prolonged boiling or by the action of a small quantity of hydrobromic acid :

$$(CH_3)_2:C:CH\cdot CH_2\cdot COOH \longrightarrow \begin{array}{l}(CH_3)_2:C\text{—}CH_2\text{—}CH_2\\ \qquad\quad\;\; |\qquad\qquad |\\ \qquad\quad\;\; O\text{————}CO\end{array}$$

Pyroterebic acid is a colourless liquid solidifying at $-15°$ and boiling at $207°$; it is lighter than water, which dissolves it with difficulty.

γ-ALLYLBUTYRIC ACID (1-Heptenoic-7 Acid), $CH_2:CH\cdot[CH_2]_4\cdot CO_2H$, is obtained from *cycloheptanone* (or *suberone*) by *Wallach's reaction*, passing through the oxime, amine, &c. :

$$\begin{array}{l}CH_2\cdot CH_2\cdot CH_2\diagdown\\ |\qquad\qquad\qquad\quad >CO\\ CH_2\cdot CH_2\cdot CH_2\diagup\end{array} \longrightarrow \begin{array}{l}CH_2\cdot CH_2\cdot CH\cdot{}_2COOH\\ |\\ CH_2\cdot CH:CH_2\end{array}$$

Cycloheptanone — γ-Allylbutyric acid

It is a liquid boiling at $226°$ and, on oxidation, is converted into *adipic acid*, $COOH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot COOH$.

TERACRYLIC ACID (2 : 3-Dimethyl-2-pentenoic-5 Acid), $(CH_3)_2:C:C(CH_3)\cdot CH_2\cdot COOH$, is homologous with pyroterebic acid and is also obtained by distilling an oxidation product (*terpenylic acid*) of oil of turpentine :

$$\begin{array}{l}\qquad\quad CH_2\cdot CO_2H\\ \qquad\quad |\\ (CH_3)_2:C\cdot CH\cdot CH_2\\ \qquad\quad |\qquad\;\; |\\ \qquad\quad O\text{——}CO\end{array} \;=\; CO_2 + (CH_3)_2:C:C(CH_3)\cdot CH_2\cdot CO_2H.$$

Terpenylic acid — Teracrylic acid

It is a liquid, b.pt. $218°$, and is slightly soluble in water ; with HBr it forms *heptalactone*, the γ-position of the double linking being thus confirmed.

CITRONELLIC ACID (Dextro-rotatory), $C_{10}H_{18}O_2$. It has not yet been definitely decided which of the two following formulæ must be attributed to this acid :

$$\begin{matrix}CH_3\diagdown\\ CH_2\!\diagup\!\!\diagup\end{matrix}\!\!C\cdot[CH_2]_3\cdot CH(CH_3)\cdot CH_2\cdot CO_2H \text{ (2 : 6-}\textit{Dimethyl-1-octenoic-8 acid}\text{).}$$

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C:CH\cdot[CH_2]_2\cdot CH(CH_3)\cdot CH_2\cdot CO_2H \text{ (2 : 6-}\textit{Dimethyl-2-octenoic-8 acid}\text{).}$$

It is a liquid boiling at $152°$ under 18 mm. pressure, has a faint odour of capric acid and is obtained by the oxidation of *citronellal* (an aldehyde, $C_{10}H_{18}O$, abundant in ethereal oils).

One of the two formulæ must be attributed to **Rhodinic Acid** (lævo-rotatory), obtained by oxidising *rhodinol*, $C_{10}H_{20}O$.

An inactive **i-Rhodinic Acid** is also known, this being obtained by the reduction (sodium in amyl alcohol) of *geranic acid*, $(CH_3)_2:C:CHC\cdot H_2\cdot CH_2\cdot C(CH_3):CH\cdot CO_2H$, the hydrogen beingadded only at the $\alpha\beta$-double linking.

UNDECENOIC ACID, $CH_2 : CH \cdot [CH_2]_8 \cdot CO_2H$. The position of the double linking in this acid is confirmed by the fact that, on oxidation, the acid yields considerable quantities of **Sebacic Acid, $CO_2H \cdot [CH_2]_8 \cdot CO_2H$.**

It is obtained (about 10 per cent.) on distilling castor oil under reduced pressure. It forms crystals melting at 24·5° and boils unchanged at 213·5° (100 mm.). When reduced with hydrogen iodide, it gives normal undecoic acid, the non-branched character of the carbon atom chain being thus proved.

HYPOGÆIC ACID, $CH_3 \cdot [CH_2]_7 \cdot CH : CH \cdot [CH_2]_5 \cdot CO_2H$, was formerly thought to exist in *Arachis hypogæa*, but the acid there present has been shown to be another acid (arachic acid). It can be prepared by fusing stearolic acid with potash, an intermediate product with two double bonds being probably formed:

$$\underset{\text{Stearolic acid}}{CH_3 \cdot [CH_2]_7 \cdot C \vdots C \cdot [CH_2]_5 \cdot CH_2 \cdot CH_2 \cdot CO_2H} \longrightarrow$$

$$\underset{\text{Hypothetical intermediate acid}}{CH_3 \cdot [CH_2]_7 \cdot CH : CH \cdot [CH_2]_5 \cdot CH : CH \cdot CO_2H} \longrightarrow$$

$$\underset{\text{Acetic acid}}{CH_3 \cdot CO_2H} + \underset{\text{Hypogæic acid}}{CH_3 \cdot [CH_2]_7 \cdot CH : CH \cdot [CH_2]_5 \cdot CO_2H}.$$

OLEIC ACID, $C_{18}H_{34}O_2$
($CH_3 \cdot [CH_2]_5 \cdot CH : CH \cdot [CH_2]_7 \cdot CO_2H$)

This acid is very abundant in nature in the form of glyceride (*triolein*), especially in vegetable and animal oils and fats. After hydrolysis of the fat, the fatty acids are liberated and from these the oleic acid separates, as it is liquid, whilst the others are solid. Although Chevreul discovered oleic acid at the beginning of the nineteenth century, it was only in 1846 that its composition was definitely established by Gottlieb.

In the subsequent section dealing with soap and candles, the method of preparing oleic acid on a large scale (Italy imported 47,300 quintals of "oleine," of the value of £132,000, and exported 35,541 quintals, of the value of £99,500, in 1910) will be described in detail; at the present juncture, only the constitution and the methods of obtaining *pure* oleic acid will be considered. Oils rich in olein (olive oil, almond oil, lard, &c.) are hydrolysed with caustic potash in the hot, the fatty acids being separated from the transparent soap thus obtained by means of hydrochloric acid; these acids are then heated for several hours with lead oxide at 100°, and the resulting lead salts dried and extracted with ether. This solvent dissolves only the lead oleate, the oleic acid being freed from the lead by means of hydrochloric acid. The oleic acid thus obtained is purified by transforming it into the barium salt and crystallising it from dilute alcohol, or by repeatedly freezing (at − 6°, − 7°) and squeezing the solid oleic acid, which, when pure, melts at 14° and has a specific gravity of 0·900 in the liquid state; it has neither smell nor taste and, in alcoholic solution, shows no reaction towards litmus. In the air and when kept for a long time, the acid turns brown, assumes an acid reaction and taste, and undergoes partial oxidation. Under a pressure of 10 mm., it boils unchanged at 223°; it can also be distilled without alteration by means of steam superheated to 250°.

The *salts* of oleic acid (and of other high fatty acids) form the *soaps;* the alkali salts are soluble in water and separable from this by salt (NaCl), in saturated solutions of which they are completely insoluble. The calcium, barium, lead, &c., salts or soaps are insoluble in water.

The action of concentrated sulphuric acid has already been mentioned (*see* Iso-oleic Acid).

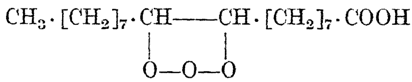
An important and characteristic reaction of oleic acid is its almost quantitative transformation, by a little nitrous acid (also by heating at 200° with sulphurous acid or sodium bisulphite), into the stereoisomeric **Elaidic Acdi,**

which separates from alcoholic solution in white scales melting at 51° to 52° and boiling unchanged at 225° under a pressure of 10 mm.[1]

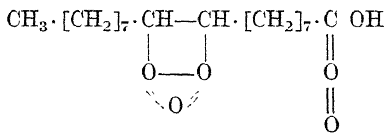
That these two isomeric acids have direct (normal) carbon-atom chains is shown with certainty by the fact that, on reduction (*e.g.* with hydriodic acid and phosphorus [2]), each of them takes up two hydrogen atoms giving stearic acid, which is known to have an unbranched carbon-atom chain; also with bromine, they give dibromo-derivatives of stearic acid, and, with permanganate, *dihydroxystearic acid*, $C_{18}H_{34}O_2(OH)_2$.

The position of the double linking in the molecule was under discussion for a number of years and until quite recently this linking was held to be at the end of the chain next the carboxyl group, *i.e.* in the $\alpha\beta$-position, $CH_3\cdot[CH_2]_{14}\cdot CH : CH\cdot COOH$, since fusion of these two acids with caustic potash resulted in the formation of palmitic acid (*Varrentrapp's reaction*, p. 290). But this proof no longer seemed sufficient when it was shown that fusion with potash generally displaced the double bond. On the other hand, *Baruch* (1894) succeeded in eliminating hydrogen bromide from the dibromide of oleic acid, thus obtaining stearolic acid, which has a triple bond in the middle of the molecule. Also the products of oxidation (by permanganate) of oleic acid consist partly of pelargonic and azelaic acids, which contain nine carbon atoms, this reaction hence indicating that the oleic acid molecule breaks in the middle of the chain, at the position of the double linking.

The most certain proof of the constitution of oleic acid has been advanced only recently as a result of the study of the *ozonide of oleic acid* and of its decomposition products (E. Molinari and Soncini, 1905 and 1906; C. Harries, 1906). The ozone is added quantitatively at the position of the double bond (*see* p. 88), and, according as ozonised air (E. Molinari) or ozonised oxygen (Harries) is employed, so the simple ozonide:



or a peroxide of the ozonide:



is obtained.

Decomposition of these *ozonides* (of oleic and elaidic acids) with dilute alkali or water in the hot results in the formation of acids (nonoic, azelaic, and others) or aldehydes (nonyl and semiazelaic) with nine carbon atoms, showing that the molecule is ruptured at the position of the central double linking.

ISO-OLEIC ACID, $C_{18}H_{34}O_2$. With concentrated sulphuric acid, elaidic and oleic acids give **Stearinsulphuric Acid, $C_{17}H_{34}(O\cdot SO_3H)\ CO_2H$,** which, with hot water, loses sulphuric acid and gives *hydroxystearic acid*, $C_{17}H_{34}(OH)\cdot CO_2H$ (with the OH at the position 10). When distilled under reduced pressure (100 mm.) or with superheated steam, this acid loses water and gives a considerable quantity of a white, solid acid—*iso-oleic acid*—which is readily soluble in alcohol and slightly so in ether, from which it crystallises in plates, melting at 44° to 45°. The addition of the molecule of water to oleic or elaidic acid should take place at the central double linking (provided the sulphuric acid does not previously displace this linking) and the subsequent separation of water should occur at two carbon atoms adjacent to the double linking, so that the probable constitution of iso-oleic acid is, $CH_3[CH_2]_8\cdot CH : CH\cdot[CH_2]_6\cdot CO_2H$. But various facts are known which throw doubt on the accuracy of this formula.

$\Delta^{\alpha\beta}$-OLEIC ACID (2-Octadecenoic-1 Acid), $CH_3\cdot[CH_2]_{14}\cdot CH : CH\cdot CO_2H$, is prepared by the removal of 1 mol. of halogen hydracid from the α-halogen derivative of stearic acid. It forms white crystals melting at 58° to 59°, does not take up ozone in cold chloroform solution, and gives palmitic acid when treated with permanganate.

[1] From an industrial point of view the transformation of a liquid fatty acid into a solid one is of interest, but this change is not utilisable in practice as it only proceeds well with fairly pure and fresh oleic acid and not with the commercial acid, which may be old and possibly polymerised (*see also later* section on Hydrolysis of Fats).

[2] According to Ger. Pats 141 029 and 211,669, 1907, the reduction can also be effected by hydrogen in presence of finely divided nickel (E. Erdmann, Sabatier and Senderens' reactions [*see* pp 34, 59, and 103; *also later*, Hydrolysis of Fats)

ERUCIC ACID (9-Docosenoic-22 Acid), $CH_3\cdot[CH_2]_7\ CH : CH\cdot[CH_2]_{11}\cdot CO_2H$, is found as glyceride in the oil of black and white mustard, and in those of grape-seed and ravison, from which it is readily extracted. It is obtained crystalline from alcohol in shining needles melting at 34°, and boils at 254·5° under a pressure of 10 mm.

It forms a lead salt soluble in ether, as does oleic acid, and, like the latter, it is readily transformed into its stereoisomeride, **Brassidic Acid**, by the action of a little nitrous acid or of sulphurous or hydrobromic acid in glacial acetic acid solution. This isomeride crystallises from alcohol in leaflets melting at 65°, and boils at 256° under a pressure of 10 mm. ; its lead salt is slightly soluble in hot ether.

These two isomerides are not reduced by sodium amalgam, but with hydriodic acid they yield the saturated behenic acid, $C_{22}H_{44}O_2$. When fused with potash, they give arachic ($C_{20}H_{40}O_2$) and acetic acids. They yield various oxidation, bromination, and esterification products. They have normal carbon-atom chains and the position of the double linking is indicated by the fact that *nonoic acid*, $CH_3\cdot[CH_2]_7\cdot COOH$, and *brassylic acid*, $CO_2H\cdot[CH_2]_{11}\cdot CO_2H$ (and also a little arachic acid), are among the products of oxidation by nitric acid, while elimination of HBr from the dibrominated product gives the corresponding *behenolic acid*, which has a triple bond and is of known constitution.

ISOERUCIC ACID, $CH_3\cdot[CH_2]_8\cdot CH : CH\cdot[CH_2]_{10}\cdot CO_2H$ (?), is obtained by adding hydrogen iodide to, and then removing it from, erucic acid (just as with *iso-oleic acid*), and it appears that the double linking is not displaced during these changes, since decomposition of the dibromide of this acid (*i.e.* elimination of HBr) gives the same behenolic acid as is given by erucic acid, while oxidation with nitric acid also gives nonoic and brassylic acids. Isoerucic acid should hence have the same constitution as erucic and brassidic acids, so that, contrary to theoretical indications, three isomerides would seem to exist ; this requires confirmation. This acid melts at 54° to 56°.

B. UNSATURATED MONOBASIC ACIDS OF THE SERIES $C_nH_{2n-4}O_2$

The members of this series may be divided into two groups, as is the case with the hydrocarbons of the diolefine and acetylene series (*see* p. 90) : acids having a triple linking (propiolic series) and those having two double linkings (diolefine series).

(a) ACIDS WITH TRIPLE LINKING

(Propiolic or Acetylenecarboxylic Series)

Name	Constitutional formula	Melting-point	Boiling-point
$C_3H_2O_2$ Acetylenecarboxylic (*propiolic*) acid	$HC \vdots C\cdot CO_2H$	9°	83° (50 mm.)
$C_4H_4O_2$ Methylacetylenecarboxylic (*tetrolic*) acid	$CH_3\ C \vdots C\ CO_2H$	76 5°	203°
$C_5H_6O_2$ Ethyl-acetylenecarboxylic acid	$C_2H_5\ C\ \ C\ CO_2H$	50°	—
$C_6H_8O_2$ Propyl- ,, ,,	$C_3H_7\ C : C\ CO_2H$	27°	125° (20 mm.)
$C_6H_8O_2$ Isopropyl- ,, ,,	$C_3H_7\ C \vdots C\cdot CO_2H$	38°	115° ,,
$C_7H_{10}O_2$ n-Butyl- ,, ,,	$C_4H_9\cdot \vdots C\cdot CO_2H$	—	135° ,,
$C_7H_{10}O_2$ tert.-Butyl- ,, ,,	$C_4H_9\ C \vdots C\ CO_2H$	47°	116° ,,
$C_8H_{12}O_2$ n-Amyl- ,, ,,	$C_5H_{11}\cdot C \vdots C\ CO_2H$	5°	149° ,,
$C_9H_{14}O_2$ n-Hexyl- ,, ,,	$C_6H_{13}\ C . C\ CO_2H$	−10°	—
$C_{10}H_{16}O_2$ n-Heptyl- ,, ,,	$C_7H_{15}\ C \vdots C\ CO_2H$	6°–10°	166° (20 mm.)
$C_{12}H_{20}O_2$ n-Nonyl- ,, ,,	$C_9H_{19}\ C \vdots C\ CO_2H$	30°	—
$C_{11}H_{18}O_2$ Dehydroundecenoic acid	$CH \vdots C\cdot[CH_2]_8\ CO_2H$	42 8°	175° (15 mm.)
$C_{11}H_{18}O_2$ Undecolic acid	$CH_3\cdot C . C[CH_2]_7\ CO_2H$	59 5°	—
$C_{18}H_{32}O_2$ Stearolic acid	$CH_3\cdot[CH_2]_7\cdot C : C\ [CH_2]_7\ CO_2H$	48°	—
$C_{18}H_{32}O_2$ Tariric acid	$CH_3\ [CH_2]_{10}\ C \vdots C\ [CH_2]_4\ CO_2H$	50 5°	—
$C_{22}H_{40}O_2$ Behenolic acid	$CH_3\ [CH_2]_7\cdot C . C\cdot[CH_2]_{11}\ CO_2H$	57·5°	—

PREPARATION. These acids can be obtained by the following reactions :

From a sodium alkyl acetylide (suspended in ether), by the action of CO_2 (*a*) or of ethyl chlorocarbonate (*b*) :

(a) $CH_3 \cdot C \vdots C \cdot Na + CO_2 = CH_3 \cdot C \vdots C \cdot CO_2Na.$
Sodium methylpropiolate

(b) $C_3H_7 \cdot C \vdots C \cdot Na + Cl \cdot CO \cdot OC_2H_5 = NaCl + C_3H_7 \cdot C \vdots C \cdot CO \cdot OC_2H_5.$
Ethyl propylacetylenecarboxylate

Various other acids of this series having the triple linking at a distance from the carboxyl group (and hence much more stable than the preceding, which, when heated, lose CO_2 and give acetylene hydrocarbons) are obtained by the elimination of 2HBr (by the action of alkali) from acids of the oleic series, this reaction being similar to that taking place with unsaturated hydrocarbons (*see* p. 91):

$$CH_3 \cdot [CH_2]_7 \cdot CHBr \cdot CHBr \cdot [CH_2]_7 \cdot CO_2H =$$
Dibromide of oleic acid

$$2HBr + CH_3 \cdot [CH_2]_7 \cdot C \vdots C \cdot [CH_2]_7 \cdot CO_2H.$$
Stearolic acid

PROPERTIES. Acids of the type $R \cdot C \vdots C \cdot CO_2H$, when treated with sodium in absolute alcoholic solution, take up 4 atoms of hydrogen, giving acids of the saturated series; they also combine easily with 2 atoms of bromine, but the second pair of bromine atoms, required to produce saturation, are added only with difficulty (the action of light facilitates the reaction); when boiled with *alcoholic* potash, they take up a molecule of water, forming saturated β-ketonic acids:

$$R \cdot C \vdots C \cdot CO_2H + H_2O = R \cdot CO \cdot CH_2 \cdot CO_2H;$$

with aqueous potash, however, they yield methyl ketones, separation of CO_2 also taking place; tert.-butyltetrolic acid does not react. The amines and hydrazine also give characteristic reactions with these acids. The esters of the acids have pleasant odours and are used in perfumes.

Acids with a triple bond do not unite with the ozone of a current of ozonised *air* (E. Molinari, 1907 and 1908), but yield peroxyozonides with ozonised *oxygen* (Harries, 1907; *see* p. 299).

PROPIOLIC ACID (Propinoic, Propargylic, or Acetylenecarboxylic Acid), $CH \vdots C \cdot CO_2H$, is obtained by heating the aqueous solution of potassium acetylenedicarboxylate:

$$\begin{array}{l} C{-}CO_2H \\ ||| \\ C{-}CO_2K \end{array} = CO_2 + \begin{array}{l} C{-}H \\ ||| \\ C \cdot CO_2K \end{array}$$

Propiolic acid is a liquid with a more intense odour than acetic acid; it has the sp. gr. 1·139, is soluble in water, alcohol, or ether, solidifies at 4°, melts at 9°, and distils unchanged at a pressure of 50 mm.

The alkali and alkaline-earth salts are extremely soluble in water.

From its esters, metallic *acetylides* (p. 91) are readily prepared. Under the action of light and in a vacuum, it undergoes partial polymerisation, yielding benzenetricarboxylic acid.

TETROLIC ACID (2-Butinoic or Methylpropiolic Acid), $CH_3 \cdot C \vdots C \cdot CO_2H$, is obtained by eliminating HCl from the β-chloro-derivative of crotonic or isocrotonic acid. It crystallises from water in rhombic plates, melting at 76·5° and boils unchanged at 203°, but it distils only with difficulty in a current of steam.

Under the action of sodium in alcoholic solution (but not with sodium amalgam in aqueous solution), it takes up hydrogen with formation of butyric acid. When oxidised with permanganate in alkaline solution, it yields acetic and oxalic acids.

DEHYDROUNDECENOIC ACID (1-Undecinoic-11 Acid), $HC \vdots C \cdot [CH_2]_8 \cdot CO_2H$, obtained by heating dibromoundecenoic acid with alcoholic potash, melts at 42·8°. On oxidation, it forms sebacic acid, $CO_2H \cdot [CH_2]_8 \cdot CO_2H$. It readily forms acetylides.

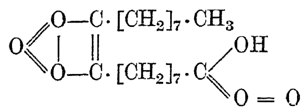
Treatment with alcoholic potash at 180° converts it into the isomeric **Undecolic Acid** (2-*undecinoic*-11 *acid*), $CH_3 \cdot C \vdots C \cdot [CH_2]_7 \cdot CO_2H$, melting at 59·5° ; the latter is hence formed with the dehydroundecenoic acid, if the reaction referred to above takes place at a high temperature. Oxidation of undecolic acid yields azelaic acid, $CO_2H \cdot [CH_2]_7 \cdot CO_2H$; it does not give acetylides, owing to the absence of the characteristic acetylenic hydrogen atom (*see* p. 90).

STEAROLIC ACID (9-Octadecinoic-1 Acid), $CH_3 \cdot [CH_2]_7 \cdot C \vdots C \cdot [CH_2]_7 \cdot CO_2H$, is readily obtained by boiling dibromostearic acid (prepared by brominating oleic or elaidic acid) with alcoholic potash. It melts at 48°, and under the influence of sulphuric acid takes up water, giving a ketostearic acid. When oxidised with permanganate, it takes up 2 atoms of oxygen, giving diketostearic acid, whilst with nitric acid it is resolved into nonoic and azelaic acids (it is, however, stable in the air, and thus differs from oleic and linolic acids) :

$$\underset{\text{Stearolic acid}}{\begin{array}{l} C-[CH_2]_7 \cdot CH_3 \\ \| \! | \\ C-[CH_2]_7 \cdot CO_2H \end{array}} \longrightarrow \underset{\text{Diketostearic acid}}{\begin{array}{l} CO \cdot [CH_2]_7 \cdot CH_3 \\ | \\ CO \cdot [CH_2]_7 \cdot CO_2H \end{array}} \longrightarrow \underset{\text{Nonoic acid}}{CH_3 \cdot [CH_2]_7 \cdot CO_2H} + \underset{\text{Azelaic acid}}{CO_2H \cdot [CH_2]_7 \cdot CO_2H}.$$

Stearolic acid unites with 2HI, and the resulting diiodostearic acid, when heated with alcoholic potash, gives stearolic acid again, but in two isomeric forms, having the triple linking in the 8 to 9 and 10 to 11 positions respectively.

The constitution of stearolic acid was confirmed by Harries (1907) by decomposing the peroxyozonide of the acid, obtained by the action of *ozonised oxygen* (ozonised air does not yield an ozonide, *see* p. 299) :


$+ 2H_2O =$

Peroxyozonide of stearolic acid

$$H_2O_2 + \underset{\text{Nonoic acid}}{CH_3 \cdot [CH_2]_7 \cdot CO_2H} + \underset{\text{Azelaic acid}}{CO_2H \cdot [CH_2]_7 \cdot CO_2H}.$$

TARIRIC ACID (6-Octadecinoic-1 Acid), $CH_3 \cdot [CH_2]_{10} \cdot C \vdots C \cdot [CH_2]_4 \cdot CO_2H$, is isomeric with stearolic acid and melts at 50·5° ; as glyceride, it forms the principal component of the fat of the fruit of *Picramnia Camboita*. It is the first compound with a triple bond resulting from the vital process of an organism. It is stable in the air and yields stearic acid on reduction with hydriodic acid, so that its molecule contains a normal carbon atom chain. Energetic oxidation with permanganate or nitric acid yields *lauric acid*, $CH_3 \cdot [CH_2]_{10} \cdot CO_2H$, and *adipic acid*, $CO_2H \cdot [CH_2]_4 \cdot CO_2H$.

BEHENOLIC ACID (9-Docosinoic-22 Acid), $CH_3 \cdot [CH_2]_7 \cdot C \vdots C \cdot [CH_2]_{11} \cdot CO_2H$, melting at 57·5°, is obtained from the dibromide of erucic or brassidic acid, in the same way as stearolic acid is formed from oleic acid. Its constitution follows from its behaviour towards reducing and oxidising agents and from the transformation of its oxime (Beckmann).

(*b*) ACIDS WITH TWO DOUBLE BONDS, $C_nH_{2n-4}O_2$

(Diolefine or Sorbine Series)

These acids are prepared synthetically by methods analogous to those used for obtaining $\alpha\beta$-unsaturated acids, for example, by treating $\alpha\beta$-unsaturated aldehydes with malonic acid in presence of pyridine :

$$\underset{\text{Acrolein}}{CH_2 : CH \cdot CHO} + CO_2H \cdot CH_2 \cdot CO_2H =$$

$$CO_2 + H_2O + \underset{\beta\text{-Vinylacrylic acid}}{CH_2 : CH \cdot CH : CH \cdot CO_2H}.$$

The acids of the sorbine series, in which the two double linkings are

conjugated—that is, one in the $\alpha\beta$- and the other in the $\gamma\delta$-position and therefore separated by a simple linking—can be reduced by sodium amalgam in aqueous solution (in presence of a stream of CO_2 to fix the alkali); only two hydrogen atoms are then added, one for each double linking, and a new double linking remains in the place of the simple linking previously separating the two original double bonds:

$$X\cdot CH : CH\cdot CH : CH\cdot CO_2H + H_2 = X\cdot CH_2\cdot CH : CH\cdot CH_2\cdot CO_2H.$$

When these sorbinic acids are oxidised with permanganate, two hydroxyl groups enter at the $\alpha\beta$-double linking, while the chain is broken at the $\gamma\delta$-double linking with formation of an aldehyde (which then undergoes oxidation) and racemic acid:

$$X\cdot CH : CH\cdot CH : CH\cdot CO_2H \longrightarrow X\cdot CHO + \underset{\text{Racemic acid}}{CO_2H\cdot CH(OH)\cdot CH(OH)\cdot CO_2H}.$$

When they are heated with aqueous ammonia, 2 mols. of the latter are added at the double linking and two diamino-acids formed.

On heating, acids of the sorbine series readily polymerise; hence, when they are heated with lime or baryta, not only is CO_2 removed and diolefine hydrocarbons obtained, but di- and tri-molecular condensation occurs, giving more complex hydrocarbons which are probably of cyclic structure.

β-**VINYLACRYLIC ACID** (1 : 3-Pentadienoic, Acid), $CH_2 : CH\cdot CH : CH\cdot CO_2H$, is synthesised by the method given above. It forms prisms showing a grey reflex, and dissolves slightly in cold water, but readily in hot. At 80° it melts to a mobile liquid, which, at 100° to 115°, becomes dense and syrupy and then suddenly decomposes with evolution of gas. In carbon disulphide solution it unites with four atoms of bromine.

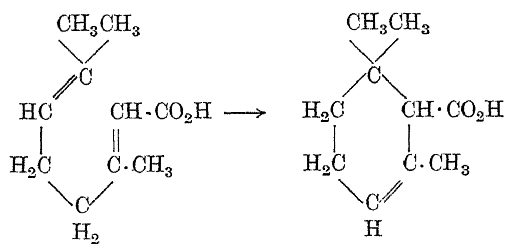
SORBINIC or SORBIC ACID (2 : 4-Hexadienoic Acid), $CH_3\cdot CH : CH\cdot CH : CH\cdot CO_2H$, occurs in considerable quantities in mountain-ash berries. It melts at 134.5°, boils at 228° with partial decomposition, is odourless and dissolves readily in alcohol or ether.

DIALLYLACETIC ACID (1 : 6-Heptadiene-4-methyloic Acid), $CH_2 : CH\cdot CH_2\cdot CH(CO_2H)\cdot CH_2\cdot CH : CH_2$, is obtained synthetically from acetoacetic acid by two separate introductions of the allyl residue. It is a liquid, sp. gr. 0.950, b.pt. 219° to 222°, and has an unpleasant smell. Oxidation with nitric acid leads to the rupture of the carbon atom chain at the two double linkings and formation of *tricarballylic acid*:

$$\begin{matrix} CO_2H\ CH_2 \\ CO_2H\ CH_2 \end{matrix}\!\!>CH\cdot CO_2H.$$

GERANIC ACID (2 : 6-Dimethyl-2 : 6-octadienoic-8 Acid), $(CH_3)_2 : C : CH\cdot CH_2\cdot CH_2\cdot C(CH_3) : CH\cdot CO_2H$, is obtained either by oxidation of the corresponding aldehyde (*citral*) with silver oxide, or by elimination of water from citraloxime by the action of acetic anhydride and hydrolysis of the resulting nitrile with alcoholic potash. It has also been obtained, by a series of reactions, from *methylheptenone*, $(CH_3)_2 : C : CH\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3$.

It is a colourless liquid of not very pleasing odour and boils at 153° under a pressure of 13 mm. When shaken with 70 per cent. sulphuric acid it yields, among other products, the isomeric α-*cyclogeranic acid*, melting at 106°:



Geranic acid α-Cyclogeranic acid

LINOLIC ACID, $C_{18}H_{32}O_2$. In the form of glyceride, this acid is an important constituent of *drying oils* (linseed, sunflower-seed, &c.). From these oils a mixture of

unsaturated fatty acids can be obtained which gives the nitrous acid reaction (solidification, owing to the formation of elaidic from oleic acid) only to a slight degree ; it contains less hydrogen but not less carbon than oleic acid and is readily oxidised and thickened by the oxygen of the air. The salts of these drying acids are still more readily oxidisable than the acids themselves, and their lead salts, like that of oleic acid, are soluble in ether. The various components of this mixture of fatty acids—with two or three double linkings —have not been completely separated, but as they fix 2 mols. of ozone (Molinari and Soncini, 1905), give a *tetrabromostearic acid*, $C_{18}H_{32}O_2Br_4$, with bromine, and with alkaline permanganate yield a *tetrahydroxystearic* (*sativic*) *acid*, $C_{18}H_{32}O_2(OH)_4$, which gives stearic acid with hydrogen iodide, the mixture must contain an acid with two double bonds. This is linolic acid, $C_{18}H_{32}O_2$, which has not been obtained pure, although its stereoisomerides—**α-Elæostearic Acid**, melting at 43° to 44°, and **Telfairic Acid**, obtained from telfairia oil, m.pt. 6° and b.pt. 220° to 225° under 13 mm. pressure—have been prepared crystalline. Distillation of ricinelaidic acid gives a further isomeride, which has a normal structure, contains two double linkings, and melts at 53° to 54°.

(c) ACIDS WITH THREE DOUBLE BONDS, $C_nH_{2n-6}O_2$

CITRYLIDENEACETIC ACID (2 : 6 - Dimethyl - 2 : 6 : 8 - decatrienoic - 10 Acid), $CH_3 \cdot C(CH_3) : CH \cdot CH_2 \cdot CH_2 \cdot C(CH_3) : CH \cdot CH : CH \cdot CO_2H$, is a mobile oil, distilling at 175° under a pressure of 18 mm., and is formed by condensing 1 mol. of citral with 1 mol. of malonic acid in presence of pyridine :

$$\underset{\text{Citral}}{CH_3 \cdot C(CH_3) : CH \cdot CH_2 \cdot CH_2 \cdot C(CH_3) : CH \cdot CHO} + \underset{\text{Malonic acid}}{CO_2H \cdot CH_2 \cdot CO_2H} = H_2O + CO_2 + \underset{\text{Citrylideneacetic acid}}{C_{12}H_{18}O_2}.$$

LINOLENIC AND ISOLINOLENIC ACIDS, $C_{18}H_{30}O_2$, are components of the mixture of drying acids, but have not yet been isolated in a pure state. But with bromine two *hexabromostearic acids*, $C_{18}H_{30}O_2Br_6$, and with permanganate two *hexahydroxystearic acids*, $C_{18}H_{30}O_2(OH)_6$, have been obtained and these must be derived from two acids containing three double bonds. The fatty acids of linseed oil contain 50 per cent. of these two acids, together with linolic and oleic acids, whilst the other drying oils contain linolic acid in preponderating amount.

The constitution of **Linolenic Acid** was definitely established by E. Erdmann, Bedford, and Raspe (1909) by decomposing the corresponding tri-ozonides. The three double bonds occur in a normal chain :

$$CH_3 \cdot CH_2 \cdot CH : CH \cdot CH_2 \cdot CH : CH \cdot CH_2 \cdot CH : CH \cdot [CH_2]_7 \cdot CO_2H.$$

The ozonides of two stereoisomerides were prepared, their products of decomposition being: propaldehyde, malonic dialdehyde, and azelaic semialdehyde.

Fish oil contains another isomeride, **Jecorinic Acid**, $C_{18}H_{30}O_2$, which has been little studied.

III. POLYBASIC FATTY ACIDS

A. SATURATED DIBASIC ACIDS, $C_nH_{2n}(CO_2H)_2$

These acids are dibasic, since they contain two carboxyl groups and form two series of derivatives : acid and normal.

In general they are crystalline substances, which distil unchanged in a vacuum (beyond C_3) and are soluble in water. The members with even numbers of carbon atoms have lower melting-points than their immediate neighbours in the series with odd numbers of carbon atoms, and the differences thus shown diminish as the number of carbon atoms increases. The solubility in water is greater with the acids containing an odd number of carbon atoms than for the others, and in both cases it diminishes with increase of molecular weight. The dissociation constant is very high for oxalic acid, and diminishes considerably in the higher homologues, which are hence less energetic acids.

TABLE OF THE NORMAL SATURATED DIBASIC ACIDS

Empirical formula	Name	Structural formula	Melting-point
$C_2H_2O_4$	Oxalic acid	COOH COOH	189° (anhyd.)
$C_3H_4O_4$	Malonic ,, ...	$CO_2H \cdot CH_2 \cdot CO_2H$	132°
$C_4H_6O_4$	Succinic ,, ...	$CO_2H \cdot [CH_2]_2\ CO_2H$	182°
$C_5H_8O_4$	Glutaric ,, ...	$CO_2H \cdot [CH_2]_3 \cdot CO_2H$	97·5°
$C_6H_{10}O_4$	Adipic ,, ...	$CO_2H \cdot [CH_2]_4 \cdot CO_2H$	149°
$C_7H_{12}O_4$	Pimelic ,, ...	$CO_2H \cdot [CH_2]_5 \cdot CO_2H$	103°
$C_8H_{14}O_4$	Suberic ,, ...	$CO_2H \cdot [CH_2]_6 \cdot OC_2H$	141°
$C_9H_{16}O_4$	Azelaic ,, ...	$CO_2H \cdot [CH_2]_7 \cdot CO_2H$	106°
$C_{10}H_{18}O_4$	Sebacic ,, ...	$CO_2H \cdot [CH_2]_8 \cdot CO_2H$	133°
$C_{12}H_{22}O_4$	Decamethylenedicarboxylic acid.	$CO_2H \cdot [CH_2]_{10} \cdot CO_2H$	125°
$C_{13}H_{24}O_4$	Brassylic acid	$CO_2H \cdot [CH_2]_{11} \cdot CO_2H$	112°
$C_{14}H_{26}O_4$	Dodecamethylenedicarboxylic acid	$CO_2H \cdot [CH_2]_{12} \cdot CO_2H$	123°
$C_{17}H_{32}O_4$	Roccellic acid	$CO_2H \cdot [CH_2]_{15} \cdot CO_2H$	132°

METHODS OF PREPARATION. In addition to the usual methods of oxidising monobasic fatty acids, primary hydroxy-acids, alcohols, and glycols, an important and general method consists in hydrolysing the nitriles (*see* p. 199) or cyano-derivatives of the acids, these being obtained from halogen alkyls with a less number of carbon atoms.

Dibasic acids—always of higher molecular weight—are also obtained by the condensation of 2 mols. of the esterified monopotassium salt of a lower dibasic acid by electrolysis in Hofer's apparatus :

$$\begin{array}{l} CH_2 \cdot COOC_2H_5 \\ | \\ CH_2 \cdot COOK \\ \\ CH_2 \cdot COOK \\ | \\ CH_2 \cdot COOC_2H_5 \end{array} + \begin{array}{c} H \cdot OH \\ H \cdot OH \end{array} = 2CO_2 + 2KOH + H_2 + \begin{array}{l} CH_2 \cdot COOC_2H_5 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_2 \cdot COOC_2H_5 \end{array}$$

2 mols. Potassium ethyl succinate — Ethyl adipate

PROPERTIES. The constitution is deduced from the synthesis in which compounds, especially the nitriles, of known constitution are employed. Structural isomerism commences with the acids containing four carbon atoms. Those acids which have the two carboxyls united to different carbon atoms (*i.e.* other than oxalic and malonic acids and their derivatives), in presence of dehydrating substances (PCl_5, $COCl_2$, &c.), or on heating, lose a molecule of water and form a kind of cyclic compound, known as an *internal anhydride :*

$$\begin{array}{l} CH_2 \cdot COOH \\ | \\ CH_2 \cdot COOH \end{array} = H_2O + \begin{array}{l} CH_2 \cdot CO \\ | \\ CH_2 \cdot CO \end{array}\!\!\!> O$$

Succinic acid — Succinic anhydride

$$\begin{array}{l} CH_2 \cdot COOH \\ | \\ CH_2 \\ | \\ CH_2 \cdot COOH \end{array} = H_2O + \begin{array}{lcl} CH_2 & — & CO \\ | & & | \\ CH_2 & & O \\ | & & | \\ CH_2 & — & CO \end{array}$$

Glutaric acid — Glutaric anhydride

The ready formation of these anhydrides by the reaction of the two terminal carboxyl groups (w, w') is readily explained by arranging the carbon

atoms in space (*see* p. 18 *et seq.*), with their valencies in the directions of the angles of regular tetrahedra. Thus, with *succinic acid*, which contains four carbon atoms, the two hydroxyls of the carboxyl groups are found to be moderately close together (Fig. 246), whilst in *glutaric acid* the two hydroxyls are almost superposed, so that water readily separates, forming a closed ring (Fig. 247).

Similarly the amides (*which see*) or the ammonium salts of these acids readily form *imides* (*see later*), which can be hydrolysed like the amides:

$$\begin{array}{l} CH_2 \cdot COONH_4 \\ | \\ CH_2 \cdot COOH \end{array} = 2H_2O + \begin{array}{l} CH_2 \cdot CO \diagdown \\ | \qquad\qquad\;\; NH \\ CH_2 \cdot CO \diagup \end{array}$$

Monoammonium succinate — Succinimide

OXALIC ACID (Ethandioic Acid), $\begin{array}{l} COOH \\ | \\ COOH \end{array}$ has been known from the earliest times, since it occurs frequently in nature in plants, especially in

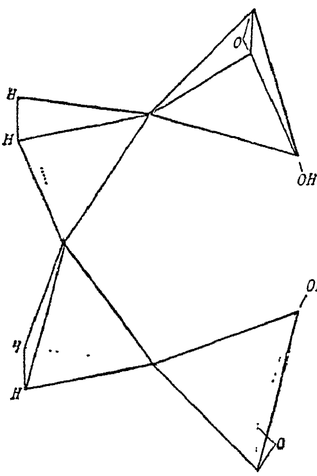


FIG. 246.

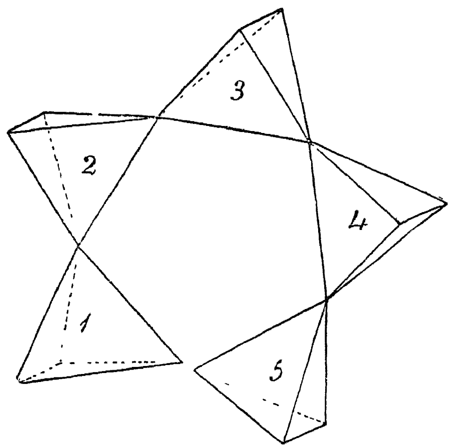


FIG. 247.

sorrel, in the form of acid potassium oxalate, and also as incrustations of calcium oxalate in plant-cells and in the roots of rhubarb.

It is often formed in the oxidation of organic substances (sugar, wood, starch, &c.) by nitric acid or permanganate, or by fused caustic potash.

It is obtained synthetically by heating sodium or potassium formate rapidly (best in a vacuum at 280°): $2H \cdot COONa = Na_2C_2O_4 + H_2$ (the reverse change, from oxalic to formic acid, has already been referred to on p. 269), or by passing carbon dioxide over metallic sodium heated to about 350°: $2Na + 2CO_2 = Na_2C_2O_4$.

Its industrial manufacture was, until recently, carried out exclusively by the method devised by Gay-Lussac in 1829 and applied by Dale in 1856: sawdust (1 part) moistened with caustic soda solution (2 parts, sp. gr. 1·4) is heated at about 240° and frequently stirred with iron plates until a greenish yellow mass is formed. While still hot, this is dissolved in water and the solution filtered and concentrated to 38° Bé. When cold, the solution deposits crude sodium oxalate, which is dissolved in a small quantity of boiling water and precipitated as insoluble calcium oxalate by means of lime. The precipitate is made into a paste with water and the oxalic acid liberated by addition of sulphuric acid. The liquid is decanted and concentrated until

the whole of the calcium sulphate separates, the oxalic acid being then allowed to crystallise out and subsequently purified by repeated recrystallisation.

At the present time, the acid and also the various alkaline oxalates are prepared by Goldschmidt's process (*see* p. 269), which consists in heating a mixture of potassium formate or carbonate with a little potassium oxalate and a slight excess of alkali (3 to 4 per cent.). From the oxalate thus obtained the oxalic acid is liberated by means of sulphuric acid.

It crystallises in odourless and transparent monoclinic prisms, $H_2C_2O_4 + 2H_2O$, which have a marked acid taste, effloresce in the air, and dissolve in 13 parts of cold or 0·3 to 0·4 part of hot water. The crystals lose their water of crystallisation partially at 30° and, after dehydration, sublime. When heated moderately strongly or treated with concentrated sulphuric acid, oxalic acid decomposes into CO, CO_2, and H_2O. It is poisonous and is used in the dyeing and printing of textiles and of wool; it serves for bleaching straw, removing rust stains from textiles, purifying glycerine and stearine, cleaning brass, &c.

The acid is estimated by means of normal caustic soda solution in presence of phenolphthalein, or of decinormal potassium permanganate solution in presence of sulphuric acid in the hot:

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = K_2SO_4 + 10CO_2 + 8H_2O + 2MnSO_4.$$

Ammoniacal impurities are detected with Nessler's reagent (vol. i, p. 539), and, when pure, the acid should leave no ash, and 0·5 grm. of it should dissolve completely when shaken with 100 c.c. of ether.

The commercial crystallised acid is sold at 56*s.* to 60*s.* per quintal, whilst the doubly purified product costs £4 and the chemically pure 128*s.* Italy imported the following quantities at 72*s.* per quintal: 1160 quintals in 1907, 960 in 1908, 755 in 1909, and 1890, costing £6424, in 1910. In Russia, four factories produced about 8500 quintals of oxalic acid in 1909, by heating sawdust with alkali. In 1908 Germany exported 51,000 quintals of oxalic acid and potassium oxalate, and 44,700 quintals in 1909. In 1911 the United States imported 1600 tons of oxalic acid of the value £33,000.

SALTS OF OXALIC ACID. Owing to the presence of two carboxyl groups in the molecule, oxalic acid gives both acid and neutral salts. The alkaline oxalates are soluble in water and are often used instead of the acid, especially in dyeing.

NORMAL POTASSIUM OXALATE, $K_2C_2O_4$, used to be obtained by neutralising the acid with potassium carbonate, concentrating and allowing to crystallise. Nowadays it is prepared by Goldschmidt's method (*see above*). It dissolves in three parts of water, crystallises with $1H_2O$ and readily effloresces in the air. It costs 84*s.* to 88*s.* per quintal, or, when chemically pure, £6.

ACID POTASSIUM OXALATE (or Potassium Hydrogen Oxalate), KHC_2O_4, is obtained by dissolving the neutral oxalate (1 mol.) and oxalic acid (1 mol.) in water, concentrating and allowing to crystallise, when it separates with $1H_2O$. It has a bitter, acid taste, is poisonous and dissolves in 14 parts of hot water.

POTASSIUM TETROXALATE (Commercial Salt of Sorrel), $KHC_2O_4 + H_2C_2O_4 + 2H_2O$, does not effloresce or lose its water of crystallisation in the air. It is obtained by mixing a hot, saturated solution of potassuim oxalate with the calculated amount of saturated oxalic acid solution. It costs 84*s.* to 88*s.* per quintal, or, if chemically pure, 128*s.*

CALCIUM OXALATE, CaC_2O_4, crystallises with $2H_2O$ and is obtained from a solution of a soluble oxalate, containing either ammonia or acetic acid, by addition of a soluble calcium salt. It is insoluble in water or acetic acid.

FERROUS OXALATE, FeC_2O_4, or, better, Ferrous Potassium Oxalate, $K_2Fe(C_2O_4)_2 + H_2O$, gives a yellow aqueous solution owing to the colour of its cation, FeC_2O_4''. It possesses strong reducing properties and is largely used on this account, while it serves also as a good photographic developer.

POTASSIUM FERRIC OXALATE, $K_2Fe_3(C_2O_4)_3$, gives a green aqueous solution owing to the colour of its cation, $Fe(C_2O_4)_3'''$. In the light it yields CO_2 and potassium ferrous oxalate, and it is used in the platinotype method of photography.

MALONIC ACID (Propandioic Acid), $H_4C_3O_4$ or $CH_2<\begin{smallmatrix}CO_2H\\CO_2H\end{smallmatrix}$, forms crystals melting at 132° and is readily soluble in water (1 : 1·4 at 15°), alcohol, or ether. It occurs in the beetroot and is obtained synthetically by hydrolysing cyanoacetic acid prepared from a hot aqueous solution of potassium chloroacetate and potassium cyanide :

$$\underset{\text{Chloroacetic acid}}{CH_2<\begin{smallmatrix}Cl\\CO_2H\end{smallmatrix}} \longrightarrow \underset{\text{Cyanoacetic acid}}{CH_2<\begin{smallmatrix}CN\\CO_2H\end{smallmatrix}} \longrightarrow \underset{\text{Malonic acid}}{CH_2<\begin{smallmatrix}CO_2H\\CO_2H\end{smallmatrix}}$$

Like all compounds containing two carboxyl groups united to the same carbon atom, it evolves CO_2 when heated above its melting-point, acetic acid being formed. Higher monobasic acids are similarly obtained from alkylated malonic acids :

$$\underset{\text{Normal propylmalonic acid}}{CH_3\cdot CH_2\cdot CH_2\ CH<\begin{smallmatrix}CO_2H\\CO_2H\end{smallmatrix}} = CO_2 + \underset{\text{Normal valeric acid}}{CH_3\cdot CH_2\cdot CH_2\ CH_2\cdot CO_2H.}$$

Malonic acid forms an ester, **ETHYL MALONATE**, $CH_2<\begin{smallmatrix}CO_2\cdot C_2H_5\\CO_2\ C_2H_5\end{smallmatrix}$, which is of great importance, since it allows of the synthetical preparation of the most varied higher dibasic acids, and from these, by loss of carbon dioxide, of the corresponding monobasic acids. This ester is obtained by passing gaseous hydrogen chloride into cyanoacetic acid dissolved in absolute alcohol ; it is then separated by distillation, as it boils at 198°. At 15° it has the sp. gr. 1·061.

The hydrogen atoms of the methylene group of this ester can be replaced by one or two atoms of sodium (or halogens) giving highly reactive *sodiomalonic esters*. The sodium in these can be substituted by one or two alkyl groups simply by treatment with an alkyl

HOMOLOGUES OF MALONIC ACID

Name of acid	Formula	Melting-point of acid	Boiling-point of the diethyl ester
Methylmalonic	$CH_3\cdot CH(CO_2H)_2$	about 130°	190°–193°
Dimethylmalonic	$(CH_3)_2 : C(CO_2H)_2$	192°–193°	196°
Ethylmalonic	$C_2H_5\cdot CH(CO_2H)_2$	112°	210°
Diethylmalonic	$(C_2H_5)_2 : C(CO_2H)_2$	124°	230°
Propylmalonic	$C_2H_5\cdot CH_2\ CH(CO_2H)_2$	93·5°	219°–222°
Dipropylmalonic	$(C_2H_5\cdot CH_2\cdot)_2 : C(CO_2H)_2$	156°	248°–250°
Isopropylmalonic	$(CH_3)_2 : CH\cdot CH(CO_2H)_2$	86°	213°–214°
Methylethylmalonic	$(CH_3)(C_2H_5)C(CO_2H)_2$	118°	207°–208°
Butylmalonic	$C_2H_5\cdot CH_2\cdot CH_2\ CH(CO_2H)_2$	98·5°	—
sec. Butylmalonic	$C_2H_5\cdot CH(CH_3)\cdot CH(CO_2H)_2$	76°	224°–225°
Isobutylmalonic	$(CH_3)_2 : CH\cdot CH_2\cdot CH(CO_2H)_2$	107°	225°–226°
Diisobutylmalonic	$[(CH_3)_2 : CH\cdot CH_2\cdot]_2C(CO_2H)_2$	145°–150°	245°–255°
Methylpropylmalonic	$(CH_3)(C_2H_5\cdot CH_2\cdot)C(CO_2H)_2$	106°–107°	220°–223°
Methylisopropylmalonic	$[(CH_3)_2CH](CH_3) : C(CO_2H)_2$	124°	221°
Pentylmalonic	$C_2H_5\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(CO_2H)_2$	82°	—
Isoamylmalonic	$(CH_3)_2CH\cdot CH_2\cdot CH_2\cdot CH(CO_2H)_2$	98°	240°–242°
Diisoamylmalonic	$[(CH_3)_2CH\cdot CH_2\cdot CH_2\cdot]_2C(CO_2H)_2$	147°–148°	278°–280°
2-Methylbutylmalonic	$(CH_3)(C_2H_5)CH\cdot CH_2\cdot CH(CO_2H)_2$	90°–91°	244°–246°
tert. Amylmalonic	$(CH_3)_2(C_2H_5)C\cdot CH(CO_2H)_2$	—	238°
sec. Amylmalonic	$(C_2H_5)_2CH\cdot CH(CO_2H)_2$	52°–53°	242°–245°
Methylisobutylmalonic	$(CH_3)_2CH\cdot CH_2\cdot C(CH_3)(CO_2H)_2$	122°	230°–235°
Ethylisopropylmalonic	$(CH_3)_2CH\cdot C(C_2H_5)(CO_2H)_2$	131°–131·5°	232°–233°
Cetylmalonic	$CH_3\cdot [CH_2]_{15}\cdot CH(CO_2H)_2$	121·5°–122°	—
Dicetylmalonic	$[CH_3\cdot (CH_2)_{15}\cdot]_2 : C(CO_2H)_2$	86°–87°	—
Dioctylmalonic	$[CH_3\cdot (CH_2)_7\cdot]_2 : C(CO_2H)_2$	75°	338°–340°

iodide, sodium iodide being separated at the same time. The resulting products are higher homologues of the malonic ester and hence yield the corresponding homologues of malonic acid on hydrolysis. The hydrolysis of the esters of dibasic acids by alkali takes place in two stages, the second ester group being hydrolysed more slowly than the first.

Treatment of ethyl malonate (1 mol.) with sodium (1 or 2 atoms) results in the evolution of hydrogen and the formation of the solid *mono-* or *di-sodiomalonic ester :*

$$Na\cdot CH\left\langle\begin{array}{l}CO_2\cdot C_2H_5\\CO_2\cdot C_2H_5\end{array}\right. \quad \text{or} \quad CNa_2\left\langle\begin{array}{l}CO_2\cdot C_2H_5\\CO_2\cdot C_2H_5\end{array}\right.$$

The sodium of the monosodio-compound can be replaced by an alkyl group and the remaining methylene hydrogen then replaced by sodium, which can subsequently be substituted by an alkyl group different from the first.

An example of this synthesis is as follows :

$$Na\cdot CH\left\langle\begin{array}{l}CO_2\cdot C_2H_5\\CO_2\cdot C_2H_5\end{array}\right. + CH_3I = NaI + CH_3\cdot CH\left\langle\begin{array}{l}CO_2\cdot C_2H_5\\CO_2\cdot C_2H_5\end{array}\right.$$

$$CH_3\cdot CNa\left\langle\begin{array}{l}CO_2\cdot C_2H_5\\CO_2\cdot C_2H_5\end{array}\right. + C_2H_5I = NaI + CH_3\cdot C(C_2H_5)\left\langle\begin{array}{l}CO_2\cdot C_2H_5\\CO_2\cdot C_2H_5\end{array}\right.$$

Hydrolysis of the final ester yields **Methylethylmalonic Acid.**

Homologues of succinic acids can be obtained as follows :

$$\underset{\text{Ethyl sodiomethylmalonate}}{CH_3\cdot CNa\left\langle\begin{array}{l}CO_2\cdot C_2H_5\\CO_2\cdot C_2H_5\end{array}\right.} \quad + \quad \underset{\text{Ethyl }\alpha\text{-bromopropionate}}{Br\cdot CH\left\langle\begin{array}{l}CO_2\cdot C_2H_5\\CH_3\end{array}\right.} \quad =$$

$$NaBr + CH_3\cdot\begin{array}{c}CO_2\cdot C_2H_5\\|\\C\\|\\CO_2\cdot C_2H_5\end{array}\cdot CH\left\langle\begin{array}{l}CO_2\cdot C_2H_5\\CH_3\end{array}\right.$$

When this complex ester is saponified and the acid thus formed heated to expel CO_2 from one of the carboxyl groups united to the same carbon atom, symmetrical dimethylsuccinic acid is obtained :

$$CH_3\cdot\begin{array}{c}CO_2H\\|\\C\\|\\CO_2H\end{array}\cdot CH\left\langle\begin{array}{l}CO_2H\\CH_3\end{array}\right. = CO_2 + CH_3\cdot\begin{array}{c}CO_2H\\|\\CH\end{array}\!\!-\!\!-\!\!\begin{array}{c}CO_2H\\|\\CH\end{array}\cdot CH_3$$

Also 2 mols. of ethyl sodiomethylmalonate (or ethyl sodiomalonate or its homologues) can be condensed in ethereal solution by means of bromine or iodine :

$$2CH_3\cdot CNa\left\langle\begin{array}{l}CO_2\cdot C_2H_5\\CO_2\cdot C_2H_5\end{array}\right. + I_2 = 2NaI + CH_3\cdot\begin{array}{c}CO_2\cdot C_2H_5\\|\\C\\|\\CO_2\cdot C_2H_5\end{array}\!\!-\!\!-\!\!-\!\!\begin{array}{c}CO_2\cdot C_2H_5\\|\\C\\|\\CO_2\cdot C_2H_5\end{array}\cdot CH_3$$

Ethyl dimethylethanetetracarboxylate

Hydrolysis of this ester gives the corresponding acid and the latter loses $2CO_2$ on heating, yielding dimethylsuccinic acid. Similarly, succinic acid may be obtained from ethyl sodiomalonate, and homologous, symmetrical alkylsuccinic acids by condensing 2 mols. of ethyl sodioalkylmalonate containing alkyl groups higher than methyl :

$$CH_3\cdot\begin{array}{c}CO_2H\\|\\C\\|\\CO_2H\end{array}\!\!-\!\!-\!\!-\!\!\begin{array}{c}CO_2H\\|\\C\\|\\CO_2H\end{array}\cdot CH_3 = 2CO_2 + CH_3\cdot\begin{array}{c}CO_2H\\|\\CH\end{array}\!\!-\!\!-\!\!\begin{array}{c}CO_2H\\|\\CH\end{array}\cdot CH_3$$

Dimethylsuccinic acid

SUCCINIC ACIDS, $C_4H_6O_4$ (Two Isomerides)

(*a*) ORDINARY SUCCINIC ACID (Butandioic or Ethylenesuccinic Acid), $CO_2H\cdot CH_2\cdot CH_2\cdot CO_2H$, occurs in nature in various plants, in the unripe grape, in certain lignites, and, more especially, in amber, from which it is obtained by distillation or fermentation.

Alcoholic fermentation also yields a small amount of succinic acid, which thus forms a normal constituent of wine. Ehrlich (1909) has shown that, in the alcoholic fermentation of sugar, the succinic acid is formed from the glutamic acid resulting from the decomposition of the cells of the ferment. Numerous syntheses also lead to the formation of succinic acid; *e g.* the reduction by hydrogen of fumaric or maleic acid, these being unsaturated dibasic acids, $C_4H_4O_4$; hydrolysis of ethylene cyanide, $CN\cdot CH_2\cdot CH_2\cdot CN$, obtained from ethylene bromide, $C_2H_4Br_2$ (*see above*); reduction of the hydroxy-acids, malic and tartaric acids, by means of hydriodic acid; heating of ethyl ethanetricarboxylate above its melting-point:

$$\begin{array}{l} CH{<}^{CO_2H}_{CO_2H} \\ | \\ CH_2\cdot CO_2H \end{array} = CO_2 + \begin{array}{l} CH_2\cdot CO_2H \\ | \\ CH_2\cdot CO_2H \end{array}$$

Various alkylsuccinic acids are obtained by syntheses with ethyl malonate.

HOMOLOGUES OF SUCCINIC ACID

Name of acid	Composition of acid	Melting-point of acid	Melting-point of the anhydride
Methylsuccinic	$C_5H_8O_4$	112°	37°
Ethylsuccinic	$C_6H_{10}O_4$	99°	Liquid
symm. Dimethylsuccinic (fumaroid)	$C_6H_{10}O_4$	209°	43°
„ „ (maleinoid)	$C_6H_{10}O_4$	129°	91°
asymm. „	$C_7H_{12}O_4$	140°–141°	31°
Propylsuccinic	$C_7H_{12}O_4$	91°	Liquid
Isopropylsuccinic	$C_7H_{12}O_4$	114°	„
symm. Methylethylsuccinic (fumaroid)	$C_7H_{12}O_4$	180°	—
„ „ (maleinoid)	$C_7H_{12}O_4$	101°–102°	Liquid
asymm. „	$C_7H_{12}O_4$	104°	„
Trimethylsuccinic	$C_7H_{12}O_4$	152°	38°
Butylsuccinic	$C_8H_{14}O_4$	81°	—
Isobutylsuccinic	$C_8H_{14}O_4$	109°	Liquid
symm. Methylpropylsuccinic (fumaroid)	$C_8H_{14}O_4$	158°–160°	„
„ „ (maleinoid)	$C_8H_{14}O_4$	92°–93°	„
„ Methylisopropylsuccinic (fumaroid)	$C_8H_{14}O_4$	174°–175°	46°
„ „ (maleinoid)	$C_8H_{14}O_4$	125°–126°	Liquid
„ Diethylsuccinic (fumaroid)	$C_8H_{14}O_4$	189°–190°	„
„ „ (maleinoid)	$C_8H_{14}O_4$	129°	„
asymm. „	$C_8H_{14}O_4$	86°	„
$\alpha\alpha$-Dimethyl-α-ethylsuccinic	$C_8H_{14}O_4$	139°–140°	„
Tetramethylsuccinic	$C_8H_{14}O_4$	200°	147°
Isoamylsuccinic	$C_9H_{16}O_4$	75°–76°	—
n-Hexylsuccinic	$C_{10}H_{18}O_4$	87°	57°
symm. Dipropylsuccinic (fumaroid)	$C_{10}H_{18}O_4$	182°–183°	Liquid
„ „ (maleinoid)	$C_{10}H_{18}O_4$	119°–121°	„
n-Heptylsuccinic	$C_{11}H_{20}O_4$	90°–91°	—
symm. Diisobutylsuccinic (fumaroid)	$C_{12}H_{22}O_4$	195°	Liquid
„ „ (maleinoid)	$C_{12}H_{22}O_4$	97°–98°	„
Tetraethylsuccinic	$C_{12}H_{22}O_4$	149°	86°
Tetrapropylsuccinic	$C_{16}H_{30}O_4$	137°	—

Pure succinic acid crystallises in monoclinic plates, m.pt. 182°, b.pt. 235°, having a disagreeable acid taste. When subjected to distillation, it loses water and yields *succinic anhydride.* Its solubility in water is 1 : 20 at the ordinary temperature, and it is highly resistant to the action of oxidising agents.

Calcium succinate is soluble in water ; *ferric succinate* is used in the estimation of iron.

(*b*) ISOSUCCINIC ACID (Ethylidenesuccinic or Methylpropandioic Acid), $CH_3\cdot CH{<}^{CO_2H}_{CO_2H}$, forms needles or prisms which melt at 130° with evolution of CO_2 and formation of propionic acid. It is more soluble in water than its isomeride, but yields no anhydride. It is obtained by synthesis from ethyl malonate, or by treatment of α-bromopropionic acid with KCN and subsequent hydrolysis.

PYROTARTARIC ACIDS, $C_5H_8O_4$ (Four Isomerides)

(*a*) GLUTARIC ACID (Normal Pyrotartaric or Pentadioic Acid), $CO_2H\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO_2H$, forms crystals melting at 97·5° and is readily soluble in water. It is obtained from 1 mol. of methylene iodide and 2 mols. of ethyl sodiomalonate, the intermediate product being hydrolysed and 2 mols. of CO_2 then eliminated by heating :

$$2Na\cdot CH{<}^{CO_2\cdot C_2H_5}_{CO_2\cdot C_2H_5} + CH_2I_2 = 2NaI + \begin{array}{l} CH{<}^{CO_2\cdot C_2H_5}_{CO_2\cdot C_2H_5} \\ | \\ CH_2 \\ | \\ CH{<}^{CO_2\cdot C_2H_5}_{CO_2\cdot C_2H_5} \end{array}$$

$$\begin{array}{l} CH{<}^{CO_2H}_{CO_2H} \\ | \\ CH_2 \\ | \\ CH{<}^{CO_2H}_{CO_2H} \end{array} = 2CO_2 + \underset{\text{Glutaric acid}}{\begin{array}{l} CH_2\cdot CO_2H \\ | \\ CH_2 \\ | \\ CH_2\cdot CO_2H \end{array}}$$

(*b*) PYROTARTARIC ACID (Methylbutandioic Acid),

$$\begin{array}{l} CO_2H\cdot CH_2\cdot CH\cdot CO_2H \\ \qquad\qquad\quad | \\ \qquad\qquad\quad CH_3 \end{array}$$

is formed, together with pyruvic acid, when ordinary tartaric acid is subjected to dry distillation ; synthetically it is prepared from ethyl acetoacetate. It forms small triclinic crystals melting at 117° and its anhydride is known. Since it contains an asymmetric carbon atom, it exists in two optically active stereoisomerides.

HIGHER HOMOLOGUES

The dialkylsuccinic acids (*see above*) contain two asymmetric carbon atoms and give rise to important cases of stereoisomerism. Together with the homologues of glutaric and adipic acids, they are found among the products of decomposition of the *terpenes* and hence serve to establish the composition of these.

β-METHYLADIPIC ACID, $CO_2H\cdot CH_2\cdot CH(CH_3)\cdot CH_2\cdot CH_2\cdot CO_2H$, melts at 85° and occurs along with menthol, &c., in the oxidation products of numerous ethereal oils.

AZELAIC ACID, $CO_2H\cdot[CH_2]_7\cdot CO_2H$, is now obtained easily and cheaply by decomposing the ozonides of oils and of the corresponding unsaturated fatty acids, especially of oleic acid (E. Molinari, Soncini, and Fenaroli, 1906–1908). The acid originally cost £24 per kilo, but can now be sold for a few shillings. It is obtained well crystallised from benzene or from water, in which it dissolves easily in the hot but only slightly in the cold (1·648 per cent. at 55°, 0·817 per cent. at 44·5°, 0·214 per cent. at 22°, and 0·212 per cent. at 15°); it is soluble also in alcohol or ether, melts at 106°, and gives a calcium salt which dissolves in cold but not in hot water.

HIGHER HOMOLOGUES OF OLEFINEDICARBOXYLIC ACIDS

Name of Acid	Structure $X = CO_2H$	Melting-point of acid	Melting-point of the anhydride	Boiling-point of the anhydride
Dimethylfumaric (α-methylmesaconic)	$CH_3\ CX\,.\,CX\ CH_3$	239°–240°	—	—
Ethylfumaric (γ-methylmesaconic) . . .	$CH_3\ CH_2\ CX\,.\,CHX$	194°–196°	—	—
Ethylmaleic (γ-methylcitraconic) . .	$CH_3\ CH_2\ CX : CHX$	100°	Liquid	229°
α-Methylitaconic . . .	$CH_2\,.\,CX\ CHX\ CH_2$	150°–151°	62°–63°	—
γ-Methylitaconic . . .	$CH_3\ CH : CX\ CH_2X$	166°–167°	—	—
Propylfumaric . .	$CH_3\ CH_2\ CH_2\ CX : CHX$	174°–175°	—	—
Propylmaleic .	$CH_3\cdot CH_2\ CH_2\ CX : CHX$	93°–95°	—	243°–245°
γ-Ethylitaconic . .	$CH_3\ CH_2\ CH_2 : CX\ CH_2X$	162°–167°	—	—
Allylsuccinic . . .	$CH_2 : CH\ CH_2\ CHX\ CH_2X$	92°–93°	Liquid	About 20°
Isopropylfumaric. .	$(CH_3)_2CH\ CX : CHX$	185°–186°	—	—
Isopropylmaleic . . .	$(CH_3)_2CH\cdot CX\cdot CHX$	91°–93°	+5°	138° (61 mm)
γγ-Dimethylitaconic (teraconic)	$(CH_3)_2C : CX\ CH_2X$	160°–161°	44°	197° (22 mm.)
γ-Methylene-γ-methylpyrotartaric	$CH_2\,.\,C(CH_3)\ CHX\ CH_2X$	146°–147°	Liquid	—
Methylethylmaleic . .	$CH_3\ CH_2\ CX : CX\ CH_3$	—	,,	230°
α-Ethylitaconic . . .	$CH_2 : CX\ CHX\ CH_2\ CH_3$	150°	52°	—
αγ-Dimethylitaconic . .	$CH_3\ CH : CX\ CHX\ CH_3$	202°	Liquid	131° (16 mm.)
αα-Dimethylitaconic . .	$CH_2 : CX\ CX(CH_3)_2$	142 5°	,,	210°–215°
Butylfumaric . . .	$C_2H_5\cdot CH_2\ CH_2\ CX : CHX$	170°	—	—
Butylmaleic . . .	$C_2H_5\ CH_2\ CH_2\ CX\ \ CHX$	80°	—	—
γ-Propylitaconic . . .	$C_2H_5\cdot CH_2\ CH : CX\ CH_2X$	159°–160°	—	—
Isobutylfumaric . .	$(CH_3)_2CH\ CH_2\cdot CX : CHX$	183°	—	—
Isobutylmaleic . . .	$(CH_3)_2CH\ CH_2\ CX : CHX$	78°–81°	—	—
γ-Isopropylitaconic . .	$(CH_3)_2CH\ CH\,.\,CX\ CH_2X$	189°–192 °	—	—
Methylpropylmaleic . .	$CH_3\ CH_2\cdot CH_2\cdot CX\,.\,CX\ CH_3$	—	Liquid	241°–242°
Methylisopropylmaleic .	$(CH_3)_2CH\ CX : CX\ CH_3$	—	,,	240°–242°
Diethylmaleic . . .	$C_2H_5\ CX : CX\cdot C_2H_5$	—	,,	239°–240°
γ-Methyl-α-ethylitaconic .	$CH_3\ CH : CX\ CHX\ C_2H_5$	136°	,,	143° (12 mm)

B. UNSATURATED DIBASIC ACIDS

I. OLEFINEDICARBOXYLIC ACIDS, $C_nH_{2n-4}O_4$

$C_4H_4O_4$	Fumaric acid . .	$\begin{array}{l} CO_2H\cdot CH \\ \quad\ \ \| \\ \quad\ \ CH\cdot CO_2H \end{array}$	melts at 200°	(sublimes)
,,	Maleic acid . . .	$\begin{array}{l} HC\ CO_2H \\ \| \\ HC\cdot CO_2H \end{array}$	,, 130°	boils at 160°
$C_5H_6O_4$	Mesaconic acid . .	$\begin{array}{l} CO_2H\cdot C\cdot CH_3 \\ \quad\ \ \| \\ \quad\ \ CH\cdot CO_2H \end{array}$	,, 202°	—
,,	Citraconic acid . .	$\begin{array}{l} CH_3\cdot C\cdot CO_2H \\ \quad\ \| \\ \quad\ CH\cdot CO_2H \end{array}$	,, 91°	—
,,	Itaconic acid .	$\begin{array}{l} CH_2 : C\cdot CO_2H \\ \quad\ \ \vert \\ \quad\ \ CH_2\cdot CO_2H \end{array}$	,, 161°	—
,,	Glutaconic acid .	$CO_2H\ CH : CH\cdot CH_2\cdot CO_2H$	,, 132°	—
$C_6H_8O_4$	Pyrocinchonic acid	$\begin{array}{l} CH_3\cdot C\cdot CO_2H \\ \quad\ \| \\ CH_3\cdot C\cdot CO_2H \end{array}$	—	—
$C_6H_6O_3$	Pyrocinchonic anhydride .	$\begin{array}{l} CH_3\cdot C\text{—}CO\diagdown \\ \quad\ \| \qquad\quad O \\ CH_3\cdot C\text{—}CO\diagup \end{array}$	,, 96°	boils at 223°
$C_6H_8O_4$	αβ-Hydromucic acid	$CO_2H\cdot CH_2\cdot CH_2\cdot CH : CH\cdot CO_2H$	,, 169°	(stable)
,,	βγ- ,, ,,	$CO_2H\cdot CH_2\cdot CH : CH\cdot CH_2\cdot CO_2H$	,, 195°	(labile)

As far as the carboxyl groups are concerned, these acids have chemical properties similar to those of the saturated dibasic acids (*see* p. 305), whilst as they are unsaturated compounds, they are able to combine with 2 atoms of hydrogen or halogen or with 1 mol. of a halogen hydracid.

They are usually prepared from the mono- and di-halogen substitution products of succinic acid and its homologues by removing either 1 mol. of halogen hydracid (by heating with KOH) or 2 atoms of halogen :

$$\begin{array}{l} CH_2\cdot CO_2H \\ | \\ CHBr\cdot CO_2H \\ \text{Monobromosuccinic acid} \end{array} \longrightarrow \begin{array}{l} HBr + CO_2H\cdot CH \\ \qquad\qquad\quad \| \\ \qquad\qquad\quad CH\cdot CO_2H \\ \qquad\qquad\quad \text{Fumaric acid} \end{array}$$

Distillation of the saturated dibasic hydroxy-acids results in the removal of 1 mol of H_2O and the formation of unsaturated acids.

The most interesting cases of stereoisomerism were considered on p. 21. When fumaric acid is either heated or treated with PCl_5, $POCl_3$, or P_2O_5, it is converted into maleic anhydride. Maleic acid is transformed into fumaric acid by heating at 200° in a sealed tube or by the action of bromine or of various acids in presence of sunlight.

FUMARIC ACID (trans-Butendioic Acid), $C_4H_4O_4$ or $\begin{array}{l} CO_2H\cdot CH \\ \qquad\quad \| \\ \qquad\quad HC\cdot CO_2H \end{array}$, forms small white prisms which have a marked acid taste and are almost insoluble in water ; it does not melt but sublimes at about 200°, subsequently losing water and becoming converted largely into maleic anhydride.

It is moderately widespread in certain vegetable organisms, *e.g.* in fungi, truffles, Iceland moss, and especially in *Fumaria officinalis*. It can be prepared by the ordinary synthetical methods and also by the action of phosphorus and bromine on succinic acid, the product obtained being decomposed by heating with water.

It is stereoisomeric with maleic acid (*see* p. 21) and its reduction to normal succinic acid by means of nascent hydrogen confirms its constitution, which is also deduced from the decomposition of the corresponding ozonide (Harries).

The **Silver Salt**, $C_4H_2O_4Ag_2$, is slightly soluble in water, and the same is the case with the barium salt, $C_4H_2O_4Ba + 3H_2O$, which in boiling water becomes insoluble and separates in the anhydrous form, $C_4H_2O_4Ba$.

MALEIC ACID (cis-Butendioic Acid), $C_4H_4O_4$ or $\begin{array}{l} CH\cdot CO_2H \\ \| \\ CH\cdot CO_2H \end{array}$ forms large prisms melting at 130° and having an unpleasant taste ; it boils at 160°, losing water and becoming converted partially into maleic anhydride. It is readily soluble in water.

Its ready transformation into maleic anhydride is explained by the stereochemical relations considered on p. 21 *et seq.*, and in many general methods of preparing the acid, the anhydride is first obtained.

The **Barium Salt**, $C_4H_2O_4Ba + H_2O$, is soluble in hot water, from which it crystallises well.

Electrolysis of the alkali salts of fumaric and maleic acids yields acetylene. When heated with sodium hydroxide at 100°, these two acids are converted into inactive maleic acid.

ITACONIC ACID (Methylenesuccinic Acid), $C_5H_6O_4$ or $\begin{array}{l} CH_2 : C\cdot CO_2H \\ \qquad\quad | \\ \qquad\quad CH_2\cdot CO_2H \end{array}$, is a white substance melting at 161° and non-volatile in steam. It is obtained by the action of water on its anhydride, the latter being formed by the interaction of citraconic anhydride

and water at 150°. Hydrogen converts it into pyrotartaric acid and permanganate into hydroxyparaconic acid. On electrolysis it yields *allene*, $CH_2 : C : CH_2$.

MESACONIC ACID (Methylfumaric Acid), $C_5H_6O_4$ or $\begin{array}{rcl} CO_2H\cdot & C & CH_3 \\ & \| & \\ H & C & CO_2H \end{array}$, is formed by heating citraconic or itaconic acid with water at 200° or by treatment of citraconic acid with dilute HNO_3 or concentrated NaOH, or with traces of bromine in sunlight. It is difficultly soluble in water, melts at 202°, and does not distil in steam. When electrolysed it forms *allylene*, $CH_3\cdot C : CH$, while with hydrogen it gives pyrotartaric acid and with permanganate, pyrotartaric and oxalic acids. It forms a barium salt, $C_5H_4O_4Ba + 4H_2O$.

CITRACONIC ACID (Methylmaleic Acid), $C_5H_6O_4$ or $\begin{array}{rcl} CH_3\cdot & C & \cdot CO_2H \\ & \| & \\ H & C & \cdot CO_2H \end{array}$, is formed from the corresponding anhydride and water. It melts at 91°, differs from the two preceding acids by being very soluble in water, distils in steam and readily gives the anhydride again. On electrolysis it yields *allylene*, while with hydrogen it forms pyrotartaric acid.

GLUTACONIC ACID, $C_5H_6O_4$ or $CO_2H\cdot CH : CH\cdot CH_2\cdot CO_2H$, is isomeric with the three preceding acids and is obtained by hydrolysing the corresponding ester with HCl; it melts at 132° and the hydrogen of its CH_2-group is replaceable by sodium (*see* p. 309).

Of the higher homologues of these acids mention may be made of the *alkylitaconic acids*, with which, on heating with NaOH solution, the position of the double linking changes, giving alkylmesaconic and *alkylaticonic acids* (Fittig), *e.g.* *isobutylaticonic acid* $(CH_3)_2CH\cdot CH : CH\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$, which melts at 93°; with alkalis these acids undergo the reverse change to some extent.

The calcium and barium salts of the alkylmesaconic acids are readily soluble in water, and those of the alkylitaconic acids slightly soluble.

Of these homologous acids, the following deserve mention:

PYROCINCHONIC ACID (Dimethylmaleic or Dimethylfumaric Acid), $C_6H_8O_4$ or $\begin{array}{c} CO_2H\cdot C = C\cdot CO_2H \\ \quad\ \ |\quad\ \ | \\ \quad\ CH_3\ CH_3 \end{array}$. Of the two stereoisomerides, only dimethylmaleic acid was until recently known and then only as the anhydride, namely, *pyrocinchonic anhydride* (m.pt. 96°, b.pt. 223°). Dimethylmaleic acid cannot exist in the free state, as it immediately gives up water, forming the anhydride; its esters are, however, known.

The anhydride, $\begin{array}{l} CH_3\cdot C\cdot CO \diagdown \\ \qquad \| \qquad\quad\ \ O \\ CH_3\cdot C\cdot CO \diagup \end{array}$, may be prepared in various ways, *e.g.* by distilling in steam the product of the interaction of pyrotartaric acid and sodium succinate. But a better yield is obtained by first preparing the nitrile of methylacetoacetic acid and distilling this in a vacuum.

According to A. Bischoff, the stereoisomeride, *Dimethylfumaric Acid*, $\begin{array}{rcl} CH_3\cdot & C & \cdot CO_2H \\ & \| & \\ CO_2H\cdot & C & \cdot CH_3 \end{array}$, could not, owing to stereochemical considerations, be formed in the free state. But Fittig and Kettner (1899) and also E. Molinari (1900) have succeeded in isolating it in various ways.[1] It forms white crystals, m.pt. 152°; its amido-derivatives have also been prepared.

[1] Fittig and Kettner, making use of the property of *various acids, homologous with citraconic acid, of yielding the corresponding fumaroid isomeride when simply heated with alkali*, obtained from pyrocinchonic anhydride, the two acids: one melting at 151°, to which is ascribed the constitution $\begin{array}{rcl} CH_2 : & C & CO_2H \\ & | & \\ CH_3\cdot & CH & CO_2H \end{array}$ (*β-methylitaconic acid*), and another melting at 240° and regarded as $\begin{array}{rcl} CH_3\cdot & C & CO_2H \\ & \| & \\ CO_2H\cdot & C & \cdot CH_3 \end{array}$ (*dimethylfumaric acid*). It is highly probable, for the following reasons, that the latter constitution should be attributed to the acid melting at 151°.

By a long series of investigations (1881 to 1896), Korner and Menozzi showed that, in general, *the treatment of α-amino-acids with methyl iodide in presence of caustic potash yields the corresponding betaines* (condensed alkyl-substituted amines); *but the β-amino-acids, if similarly treated, always yield the corresponding unsaturated, non-nitrogenous acids of the fumaroid type* (betaines being probably formed as intermediate products). *As the same β-amino-acid can be obtained from the two stereoisomeric unsaturated acids, this general reaction renders it possible to pass from a malenoid unsaturated acid to the corresponding fumaroid stereoisomeride* By applying this reaction to pyrocinchonic anhydride, E. Molinari arrived at the expected stereoisomeride (*dimethylfumaric acid*), melting at 152°.

Bauer (1904) made the interesting observation that dimethylfumaric acid and, in general, compounds containing carboxyl or alkyl or phenyl groups or bromine atoms united to two carbon atoms connected by a double linking *do not unite with bromine.*

HYDROMUCONIC ACIDS, $C_6H_8O_4$. Of these are known (1) the $\alpha\beta$-unsaturated acid, $CO_2H \cdot \overset{\delta}{C}H_2 \cdot \overset{\gamma}{C}H_2 \cdot \overset{\beta}{C}H : \overset{\alpha}{C}H \cdot CO_2H$, which is *stable* and melts at 169° ; with permanganate it yields succinic acid. (2) The *unstable* $\beta\gamma$-acid, $CO_2H \cdot CH_2 \cdot CH : CH \cdot CH_2 \cdot CO_2H$, which melts at 195° and is obtained by reducing muconic acid ; when heated with alkali, it is converted into the stable isomeride, whilst with permanganate it gives malonic acid, $CO_2H \cdot CH_2\ CO_2H$.

Of the **DIOLEFINEDICARBOXYLIC ACIDS,** only **Muconic Acid,** $CO_2H \cdot CH : CH \cdot CH : CH\ CO_2H$, melting above 260°, need be referred to.

Of the **ACETYLENEDICARBOXYLIC ACIDS,** mention will be made only of **Acetylenedicarboxylic (Butindioic) Acid,** $CO_2H\ C \vdots C \cdot CO_2H$, which melts and decomposes at 175° ; it crystallises with $2H_2O$. It is obtained on removing HBr from dibromo- or isodibromo-succinic acid by means of potash.

Diacetylenedicarboxylic Acid, $CO_2H \cdot C \vdots C\ C \vdots C\ CO_2H + H_2O$, turns dark red in the light and explodes at 177°. When reduced with sodium amalgam, it yields hydromuconic acid.

Tetracetylenedicarboxylic Acid, $CO_2H\ C \vdots C \cdot C \vdots C \cdot C \vdots C \cdot C \vdots C \cdot CO_2H$, forms white crystals which blacken rapidly in the light and explode violently on heating.

C. TRIBASIC ACIDS

These have usually been obtained synthetically and are not very stable since they readily yield carbon dioxide and dibasic acids on heating ; their esters, however, exhibit increased stability. Their properties and methods of preparation vary according as the carboxyl groups are united to one or to various carbon atoms.

Of the many such acids known, the following may be mentioned :

TRICARBALLYLIC ACID (symm. $\alpha\alpha\omega$- **Propanetricarboxylic** or **Pentanedioic-3-methyloic Acid**),

$$\begin{array}{l} CH_2 \cdot CO_2H \\ | \\ CH \cdot CO_2H \\ | \\ CH_2\ CO_2H \end{array}$$

occurs in the deposits left on concentrating beet-sugar juices *in vacuo*. Synthetically it is obtained by converting glycerol into the tribromohydrin or allyl tribromide, which is treated with potassium cyanide to give the corresponding tricyano-compound, the latter being then hydrolysed to tricarballylic acid ; the constitution of the acid is thus proved. This acid forms white, prismatic crystals melting at 166°. It can also be prepared by reducing unsaturated tricarboxylic acids (*e.g.* aconitic acid).

CAMPHORONIC ACID ($\alpha\alpha\beta$-**Trimethylcarballylic Acid**),

$$\begin{array}{ccccc} & CO_2H & & CO_2H & CO_2H \\ & | & & | & | \\ CH_3 \cdot & C & — & C & — CH_2 \\ & | & & | & \\ & CH_3 & & CH_3 & \end{array}$$

is formed on oxidising camphor, of which it serves to indicate the constitution ; it melts at 135°.

ACONITIC ACID is an unsaturated tribasic acid of the constitution $CO_2H \cdot CH_2 \cdot C(CO_2H) : CH \cdot CO_2H$, and is found in beetroot, sugar-cane, *Aconitum napellus,* &c. It is obtained synthetically by eliminating CO_2 from citric acid by the action of heat or of various reagents. It melts at 191°, losing CO_2, and forming itaconic anhydride. It dissolves readily in water and with nascent hydrogen generates tricarballylic acid, its structure being indicated by this reaction.

*

D. TETRABASIC ACIDS

These are formed from ethyl sodiomalonate (*see* p. 309) by means of an unsaturated ester, *e.g.* of fumaric acid. When heated, they lose CO_2, forming tribasic and, better, dibasic acids.

Olefinetetracarboxylic Acids are also known.

FF. DERIVATIVES OF THE ACIDS

I. HALOGEN DERIVATIVES

One or more of the hydrogen atoms of an alkyl group united with carboxyl can be replaced by halogens, the carboxyl group being left intact. The *halogen derivatives of the acids*, thus obtained, are more markedly acid in character than the original substances. They are obtained by the action of chlorine or bromine in sunlight or, better, by heating the acid with the halogen in presence of a little water or sulphur.

On the other hand, the hydroxyl of the carboxyl group can be replaced, forming *acid halides :* $-CO-X$ (by treating the acid with phosphorus chloride or bromide). That the halogen has replaced the hydroxyl group is shown by the fact that these acid halides yield the original acids when treated with cold water, whilst halogens are not displaced from alkyl residues in this way. These acid chlorides and bromides readily give the monochloro- and monobromo- acids when treated further with chlorine or bromine.

(*a*) HALOGENATED ACIDS

When the carbon atom (*a*), to which the carboxyl group is attached, is not united directly with hydrogen [*e g.* in trimethylacetic acid, $(CH_3)_3C \cdot CO_2H$], bromine is not taken up (*see* p. 315). The constitution of a halogenated acid, or rather the position of the halogen atom, is deduced from that of the corresponding *hydroxy-acid* (containing a hydroxyl group in place of the halogen) obtained by heating the halogenated acid with sodium carbonate solution or with water and lead oxide.

On the other hand, the passage from hydroxy-acid to the corresponding halogenated acid can be effected by treatment with phosphorus chloride or bromide.

The acid character becomes more marked on passing from the iodo- to the bromo- and then to the chloro-compounds and also increases with the number of halogen atoms in the molecule.

While the α-halogenated acids readily yield the corresponding hydroxy-acids, the β-acids yield the corresponding unsaturated acids (*see* p. 292) and may even lose CO_2, giving unsaturated hydrocarbons. But the γ-halogenated acids, when heated with sodium carbonate solution or with water alone, give up a molecule of halogen hydracid and yield, not the unsaturated acids, but *lactones* (*see* p. 295).

When halogenated acids are prepared by the interaction of an unsaturated acid with a halogen hydracid (*e g.* HI), the halogen becomes attached to the least hydrogenated carbon atom (*see* p. 96). Thus, with a $\Delta^{\alpha\beta}$-acid, where the double linking is between the α- and β-carbon atoms, the halogen unites with the latter.

The halogenated and poly-halogenated acids exhibit isomerism, since the halogen atom may be joined to the α, β, γ, &c., carbon atom, or several halogen atoms may be united with one and the same carbon atom or with different ones.

When heated with potassium cyanide, the mono-haloid acids yield *cyano acids* :

$$\underset{\text{Potassium chloroacetate}}{CH_2Cl\cdot COOK} + KCN = KCl + \underset{\text{Potassium cyanoacetate}}{CN\cdot CH_2\cdot COOK}.$$

With sodium sulphite they give dibasic *sulpho-acids*, the sulphonic group of which is readily replaced by hydroxyl by boiling with alkali :

$$Na_2SO_3 + Cl\cdot CH_2\cdot COONa = NaCl + \underset{\text{Sodium sulphoacetate}}{SO_3Na\cdot CH_2\cdot COONa}.$$

With reference to the affinities of the halogenated acids, *see* Note on p. 268.

MONOCHLORACETIC ACID (**Chlorethanoic Acid**), **$CH_2Cl\cdot COOH$**, is prepared by the general method, that is, by passing dry chlorine into hot acetic acid in presence of acetic anhydride, phosphorus, or sulphur. It forms rhombic crystals which corrode the flesh and melt at 62° ; on solidification an unstable modification is obtained which, for some time, melts at 52° ; it boils at 186°. When heated with water or alkali it gives **Hydroxyacetic Acid** (*glycollic acid*), $OH\cdot CH_2\cdot CO_2H$; with ammonia it yields **Amino-acetic Acid** (*glycine* or *glycocoll*), $NH_2\cdot CH_2\cdot CO_2H$.

The properties of the other halogenated acids are given in the Table on the next page.

(*b*) ACID HALIDES

Of these compounds the most important are the *chlorides* of the acid radicals, which are termed *acichlorides* or *chloranhydrides*. Although acetyl chloride, $CH_3\cdot CO\cdot Cl$, is readily obtainable, it has not been found possible to prepare *formyl chloride*, $H\cdot CO\cdot Cl$, a mixture of $CO + HCl$ being always obtained.

These compounds are usually colourless liquids which have pungent odours and fume strongly in the air, the moisture in the latter liberating hydrogen chloride. Their boiling-points are below those of the corresponding acids, and they distil without decomposing ; the higher members are, however, solid and do not distil unchanged even in a vacuum.

The principal methods for preparing these substances are as follows :

(*a*) The organic acid is heated for a short time on the water-bath with PCl_5 (with higher acids), PCl_3 (with acids below C_{10}) or, in some cases, sulphuryl chloride, SO_2Cl_2 :

$$\underset{\text{Lauric acid}}{C_{11}H_{23}\cdot CO\cdot OH} + PCl_5 = C_{11}H_{23}\cdot CO\cdot Cl + HCl + POCl_3,$$

the phosphorus oxychloride and hydrochloric acid being eliminated by distillation *in vacuo* ; or,

$$3CH_3\cdot CO\cdot OH + 2PCl_3 = 3CH_3\cdot CO\cdot Cl + 3HCl + P_2O_3,$$

the acetyl chloride thus formed being separated by distillation, the P_2O_3 being left in the residue.

(*b*) With thionyl chloride the acids yield the chloranhydrides, the other products formed at the same time being volatile and hence easily removable : $X\cdot CO\cdot OH + SOCl_2 = X\cdot CO\cdot Cl + HCl + SO_2$.

(*c*) In some cases the acid is treated simply with HCl in presence of a dehydrating agent, (P_2O_5) : $CH_3\cdot CO\cdot OH + HCl = H_2O + CH_3\cdot CO\cdot Cl$.

CHEMICAL PROPERTIES. The great reactivity of the chlorine atom of these substances renders them of considerable importance in chemical syntheses. Water, ammonia (amines), and alcohols decompose them in the cold with great violence :

$$CH_3\cdot CO\cdot Cl + H_2O = HCl + CH_3\cdot CO\cdot OH$$

$$CH_3\cdot CO\cdot Cl + NH_3 = HCl + CH_3\cdot CO\cdot NH_2 \text{ (acetamide)}$$

$$CH_3\cdot CO\cdot Cl + C_2H_5\cdot OH = HCl + CH_3\cdot CO\cdot OC_2H_5 \text{ (ethyl acetate)}.$$

HALOGEN DERIVATIVES OF THE SATURATED MONOBASIC ACIDS

Formula	Name	Melting-point.	Boiling-point	Preparation and properties
$CHCl_2 \cdot CO_2H$	Dichloroacetic acid	—	191°	By heating: $CCl_3 \cdot CHO + KCN + H_2O = CHCl_2 \cdot CO_2H + KCl + HCN$. When heated with alkali, it gives oxalic and acetic acids. The silver salt with water gives *glyoxylic acid*, $CHO \cdot CO_2H$.
$CCl_3 \cdot CO_2H$	Trichloroacetic acid	55°	195°	By oxidising chloral with nitric acid. With alkali in the hot it gives chloroform and CO_2.
$CN \cdot CH_2 \cdot CO_2H$	Cyanoacetic acid	70°	—	On hydrolysis, gives malonic acid.
$CH_3 \cdot CHCl \cdot CO_2H$	α-Chloropropionic acid	—	186°	Lactic acid + PCl_5 = $CHCl \cdot CO_2H$ (*lactyl chloride*), which with H_2O = HCl + $CH_3 \cdot CHCl \cdot CO_2H$.
$CH_2Cl \cdot CH_2 \cdot CO_2H$	β-Chloropropionic acid	41·5°	204°	Acrolein + HCl = β-chloropropaldehyde, which with HNO_3 = β-chloropropionic acid.
$CH_3 \cdot CCl_2 \cdot CO_2H$	αα-Dichloropropionic acid	—	188°	From propionic acid + Cl (similarly for the bromo-derivative).
$CH_2Cl \cdot CHCl \cdot CO_2H$	αβ-Dichloropropionic acid	50°	210°	Acrylic acid + Cl (similarly for the bromo-derivative).
$CHBr_2 \cdot CH_2 \cdot CO_2H$	ββ-Dibromopropionic acid	71°	—	β-Bromoacrylic acid + HBr.
$CH_2I \cdot CH_2 \cdot CO_2H$	β-Iodopropionic acid	82°	—	From acrylic acid + HI or from glyceric acid + phosphorus iodide.
$CH_3 \cdot CH_2 \cdot CHCl \cdot CO_2H$	α-Chloro-n-butyric acid	—	158°	
$CH_3 \cdot CHCl \cdot CH_2 \cdot CO_2H$	β-Chloro-n-butyric acid	—	—	From allyl cyanide.
$CH_2Cl \cdot CH_2 \cdot CH_2 \cdot CO_2H$	γ-Chloro-n-butyric acid	10°	—	

With organic salts they yield anhydrides :

$$CH_3\cdot CO\cdot Cl + CH_3\cdot CO\cdot ONa = NaCl + CH_3\cdot CO\cdot O\cdot CO\cdot CH_3.$$

Sodium amalgam reduces them to aldehydes and then to alcohols.

ACETYL CHLORIDE (Ethanoyl Chloride), $CH_3\cdot CO\cdot Cl$, is a liquid boiling at 51° and having the sp. gr. 1·105 at 20°. It is prepared by mixing 5 parts of glacial acetic acid and 4 parts of phosphorus trichloride in the cold, heating for a short time at 40° and, after evolution of HCl ceases, distilling the acetyl chloride and purifying it by rectification. Water decomposes it with development of heat.

It is employed in organic synthesis, since it readily yields acetyl derivatives of alcohols and of primary and secondary amines.

The commercial product costs 3*s*. to 4*s*. per kilo, and the chemically pure 14*s*.

The boiling-points of the higher homologues of acetyl chloride rise with the molecular weight and, with isomerides, that with the normal constitution has the highest boiling-point ; the specific gravity diminishes as the molecular weight increases.

Acetyl iodide boils at 108°, *propionyl chloride* at 108° (the bromide at 104° and the iodide at 127°) ; *normal butyryl chloride* boils at 101° (the bromide at 128° and the iodide at 146°) and *isobutyryl chloride* at 92° (the bromide at 116°) ; *isovaleryl chloride* boils at 114° (the bromide at 143° and the iodide at 168°) and *trimethylacetyl chloride*, $(CH_3)_3C\cdot CO\cdot Cl$, at 105°.

II. ANHYDRIDES

The anhydrides of organic acids were discovered by C. Gerhardt in 1851 and correspond with those of the inorganic acids, that is, they may be regarded as products of the condensation of 2 mols. of acid with expulsion of 1 mol. of water. And here also, the organic anhydrides, when they are at all soluble, take up water and regenerate the acids. With organic acids, however, more varied and interesting cases are presented, since 2 mols. of different acids can condense (*mixed anhydrides*), while *internal anhydrides* can be formed by condensation between the two carboxyl groups of a dibasic acid.

The anhydrides may be regarded also as oxides of acid radicals, *e.g.* acetic anhydride, $\begin{matrix}CH_3\cdot CO\\CH_3\cdot CO\end{matrix}\!\!>\!O$, or *acetyl oxide*, $(CH_3\cdot CO)_2O$.

PROPERTIES. The first members of the series are liquid, the higher ones solid ; they generally dissolve but slightly in water, their transformation into acids being very slow. They have a neutral reaction and are soluble in ether and often in alcohol.

With ammonia and the primary and secondary amines, they form *amides* and ammoniacal salts : $(CH_3CO)_2O + 2NH_3 = CH_3\cdot CO\cdot NH_2$ (acetamide) $+ CH_3\cdot CO\cdot ONH_4$ (ammonium acetate).

When heated with an alcohol, they give the corresponding ester and acid :

$$(CH_3CO)_2O + C_2H_5\cdot OH = CH_3\cdot COOC_2H_5 + CH_3\cdot COOH.$$

With halogen hydracids in the hot they yield the halides of the acids and the free acids : $(CH_3CO)_2O + HCl = CH_3\cdot CO\cdot Cl + CH_3\cdot COOH$.

Aldehydes combine with anhydrides, forming esters, while sodium amalgam reduces anhydrides to aldehydes and alcohols.

GENERAL METHODS OF PREPARATION. (*a*) By the action of acid chlorides on the dry alkali salts of the corresponding acids :

$$CH_3\cdot CO\cdot Cl + CH_3\cdot COONa = NaCl + \begin{matrix}CH_3\cdot CO\\CH_3\cdot CO\end{matrix}\!\!>\!O.$$

(*b*) The same result is obtained by the action of phosphorus oxychloride (or phosgene $COCl_2$) on a mixture of the alkali and alkaline-earth salts of the corresponding acid, the acid chloride being formed as an intermediate product.

(*c*) The higher anhydrides are obtained from the corresponding acids by the action of acetyl chloride :

$$CH_3\cdot COCl + 2X\cdot COOH = HCl + CH_3\cdot COOH + (X\cdot CO)_2O.$$

(*d*) The formation of anhydrides from the acids by the subtraction of water (by means of P_2O_5) gives low yields, the best being obtained with palmitic and stearic acids (using acetic anhydride in the hot as dehydrating agent).

The properties of the best-known anhydrides are given in the following Table :

Formula	Name	Melting-point	Boiling-point	Specific gravity
$(CH_3\cdot CO)_2O$	Acetic anhydride	—	136·5°	1·078 (at 21°)
$(C_2H_5\cdot CO)_2O$	Propionic anhydride .	—	168 6°	1·034 (at 0°)
$(C_3H_7\cdot CO)_2O$	norm. Butyric anhydride	—	192°	0·978 (at 12·5°)
,,	Isobutyric anhydride .	—	182°	0 958 (at 16·5°)
$(C_4H_9\cdot CO)_2O$	Isovaleric anhydride .	—	215°	—
,,	Trimethylacetic anhydride	—	190°	—
$(C_5H_{11}\cdot CO)_2O$	norm. Caproic anhydride	—	242°	0 928 (at 17°)
$(C_6H_{13}\cdot CO)_2O$	Œnanthic anhydride .	+17°	257°	0·912 (at 17°)
$(C_7H_{15}\cdot CO)_2O$	Caprylic anhydride .	−1°	186° (15 mm.)	—
$(C_8H_{17}\cdot CO)_2O$	Pelargonic anhydride .	+16°	207° ,,	—
$(C_{11}H_{23}\cdot CO)_2O$	Lauric anhydride . .	+41°	166° (vacuum)	—
$(C_{13}H_{27}\cdot CO)_2O$	Myristic anhydride .	+51°	198° ,,	—
$(C_{15}H_{31}\cdot CO)_2O$	Palmitic anhydride .	55°–66°	—	—
$(C_{17}H_{35}\cdot CO)_2O$	Stearic anhydride . .	72°	—	—

ACETIC ANHYDRIDE (Ethanoic Anhydride), $(CH_3\cdot CO)_2O$, is of some importance industrially owing to its formation of acetyl derivatives with alcohols or with primary or secondary amines. It is a suitable reagent for determining how many hydroxyl groups an organic substance contains (*see* Acetyl Number, p. 189). It is a colourless, very mobile liquid, sp. gr. 1·078 at 21°, b.pt. 136·5°, and has a pungent odour.

It is prepared by dropping 5 parts of acetyl chloride on to 7 parts of dry powdered sodium acetate, which is kept cool meanwhile. The mixture is subsequently gently heated for a short time and the anhydride then distilled off on a sand-bath. It is purified by redistillation in presence of a little anhydrous sodium acetate, the portion boiling at the correct temperature being collected. It is also prepared industrially by method (*b*) given above (Ger. Pats. 161,882 ; also 132,605 and 146,690).

Commercial acetic anhydride costs about £18 per quintal, and the highly purified product (puriss.) £24.

The *anhydrides of di- and poly-basic acids* are not of great importance and are considered to some extent in dealing with the corresponding acids (succinic, pyrocinchonic, &c.) ; with water they yield the acids with moderate readiness (*see* pp. 305 and 314).

III. HYDROXY-ACIDS

A. SATURATED DIVALENT MONOBASIC ACIDS

These may be regarded as derived from monobasic acids by the substitution of an atom of hydrogen (not that of the carboxyl group) by a hydroxyl group. These acids possess, at the same time, acidic and alcoholic characters and are hence termed *divalent monobasic acids* or *divalent alcohol acids.* The hydroxyl and the carboxyl groups may be substituted at the same time, the compounds then exhibiting the general properties of the acids and alcohols, in addition to new and special characters varying with the position occupied by the carboxyl relatively to the hydroxyl (*see* pp. 295 and 297).

They are usually syrups which may undergo crystallisation ; in comparison with the corresponding fatty acids, the hydroxy-acids are more soluble in water and in alcohol, but less soluble in ether. They do not distil unchanged and often lose water, forming anhydrides.

GENERAL METHODS OF PREPARATION. (*a*) By oxidising dihydric alcohols so as to transform the primary alcoholic group into carboxyl.

(*b*) By boiling unsaturated acids with sodium hydroxide, so that a molecule of water is added at the double bond.

(*c*) By substituting the halogen of a monohalogenated monobasic acid by hydroxyl ; this is effected by treatment with KOH or with silver acetate, the diacetate formed in the latter case being hydrolysed by heating with sodium carbonate :

$$\underset{\text{Monochloracetic acid}}{CH_2Cl\cdot COOH} + H_2O = \underset{\text{Glycollic acid}}{OH\cdot CH_2\cdot CO_2H} + HCl.$$

(*d*) α-Hydroxy-acids are obtained by hydrolysing the nitriles formed on treating the aldehydes or ketones (having one atom of carbon less) with hydrocyanic acid :

$$\underset{\text{Ethylidenecyanohydrin}}{CH_3\cdot CH{<}^{OH}_{CN}} + 2H_2O = NH_3 + CH_3\cdot CH(OH)\cdot COOH.$$

Glycolcyanohydrin, $OH\cdot CH_2\cdot CH_2\cdot CN$, yields ethylenelactic acid, $OH\cdot CH_2\cdot CH_2\cdot COOH$.

(*e*) By the action of nitrous acid on amino-acids :

$$\underset{\text{Glycocoll}}{COOH\cdot CH_2\cdot NH_2} + NO\cdot OH = H_2O + N_2 + COOH\cdot CH_2\cdot OH$$

(*f*) By reducing aldehydic or ketonic acids :

$$\underset{\text{Pyruvic acid}}{CH_3\cdot CO\cdot COOH} + H_2 = \underset{\text{Lactic acid}}{CH_3\cdot CH(OH)\cdot COOH.}$$

(*g*) By oxidation of acids containing a tertiary carbon atom, $>CH\cdot COOH$, with permanganate.

PROPERTIES AND CONSTITUTION. The constitutions of these acids can always be deduced from the syntheses indicated above. That they contain an alcoholic group is shown by the fact that the hydroxylic hydrogen can be replaced by an alkyl group, giving true *non-hydrolysable ethers*. Similarly the presence of a carboxyl group is shown by the formation of *hydrolysable esters*. The isomerism exhibited is the same as with the haloid derivatives of the acids.

The number of alcoholic hydroxyl groups is determined by the *acetyl number* (*see* p. 189). The reactivity, which corresponds with the dissociation constant, increases with the proximity of the hydroxyl to the carboxyl group.

α-, β-, γ-, and δ-hydroxy-acids are distinguished also by the products resulting from the elimination of one or more molecules of water.

Thus, α-hydroxy-acids, when heated, lose 2 mols. of H_2O per 2 mols. of acid, the hydroxyl group of the one reacting with the carboxyl group of the other ; the compound formed is called a *lactide* and is a double ester, which yields the acid again on hydrolysis with hot water or dilute acid :

$$\underset{\text{2 mols. Lactic acid}}{\begin{array}{l} COOH\cdot CH(OH)\cdot CH_3 \\ \\ CH_3\cdot CH(OH)\cdot COOH \end{array}} = 2H_2O + \underset{\text{Lactide}}{\begin{array}{ccc} & CO - & CH\cdot CH_3 \\ & | & | \\ & O & O \\ & | & | \\ CH_3\cdot & CH - & CO \end{array}}$$

Further, α-hydroxy-acids, if heated with sulphuric acid, yield the aldehydes or ketones from which they can originate (*see above*), formic acid being also formed.

The β-acids, however, lose only 1 mol. of water, giving unsaturated acids (*see* p. 292), while, when boiled with 10 per cent. potassium hydroxide solution, they give at the same time $\alpha\beta$- and $\alpha\gamma$- unsaturated acids—a reversible reaction leading to a position of chemical equilibrium; when heated with sulphuric acid they form acids of the acrylic series.

The γ- and δ-acids lose 1 mol. of water, yielding *lactones* (internal anhydrides):

$$\underset{\gamma\text{-Hydroxybutyric acid}}{OH\cdot CH_2\cdot CH_2\cdot CH_2\cdot COOH} = H_2O + \underset{\text{Butyrolactone}}{\underbrace{CH_2\cdot CH_2\cdot CH_2\cdot CO}_{O}}$$

which are almost always formed when attempts are made to liberate these hydroxy-acids from their salts. The lactones are neutral liquids soluble in water, alcohol, and ether; they distil unchanged and with alkali form the salts of the corresponding hydroxy-acids.

When the hydroxy-acids are heated with sulphuric acid, they furnish the corresponding fatty acids.

GLYCOLLIC ACID (**Hydroxyacetic** or **Ethanoloic Acid**), $OH\cdot CH_2\cdot COOH$, crystallises in needles or plates melting at 80°, and is soluble in water, alcohol, or ether. In nature it is found in immature eggs and in the leaves of the wild vine.

It can be obtained by the general methods given above and also by oxidising alcohol or glycol with dilute nitric acid or by reducing oxalic acid with nascent hydrogen. It is usually prepared by hydrolysing monochloracetic acid with KOH [general method (*c*)].

Of some interest is the formation of the various *anhydrides* of glycollic acid, these being formed by the removal of 1 mol. of H_2O from two mols. of the acid as follows:

(1) From the two alcohol groups, giving a true ether with two free acid groups, $O\!<\!\begin{matrix}CH_2\cdot COOH\\ CH_2\cdot COOH\end{matrix}$, *diglycollic acid*, m.pt. 148°; (2) from the two carboxyl groups; this should give the *anhydride of glycollic acid*, $\begin{matrix}OH\cdot CH_2\cdot CO\\ OH\cdot CH_2\cdot CO\end{matrix}\!>\!O$, which is not yet known; (3) from one alcohol and one acid group, giving a true ester, *glycolglycollic acid*, $\begin{matrix}OH\cdot CH_2\cdot CO\\ COOH\cdot CH_2\end{matrix}\!>\!O$. Also loss of $2H_2O$ from the two alcoholic and acidic groups gives either (1) *Diglycollic anhydride* (anhydride and ether at the same time), $O\!<\!\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CO\end{matrix}\!>\!O$ (melting at 97° and boiling at 240°), or, when each molecule of water separates from 1 alcoholic and 1 acidic group, (2) the isomeric *glycollide*, $O\!<\!\begin{matrix}CH_2\cdot CO\\ CO\cdot CH_2\end{matrix}\!>\!O$, melting at 86°.

Glycollic acid forms a *calcium salt*, $(OH\cdot CH_2\cdot COO)_2Ca + 3H_2O$, insoluble in water. The most important derivative of glycollic acid is

GLYCOCOLL (**Glycine** or **Aminoacetic** or **Aminoethanoic Acid**), $COOH\cdot CH_2\ NH_2$, which is the first member of the amino-acid series so important to vegetable physiology. It is obtained, together with secondary products, by the action of concentrated ammonia solution on monochloracetic acid:

$$CH_2Cl\cdot COOH + 2NH_3 = NH_4Cl + NH_2\cdot CH_2\cdot COOH.$$

It is always formed in the decomposition of hippuric acid (benzoylglycocoll) with HCl, or by the action of acid or alkali on gelatine.

It can also be obtained by the reduction of ethyl cyanocarboxylate by means of nascent hydrogen or from cyanogen and boiling hydriodic acid.

Its homologues are prepared synthetically in various ways, *e.g.* by treating aldehyde-ammonias with hydrocyanic acid and hydrolysing the amino-cyanides thus obtained with HCl.

Glycocoll crystallises in rhombic columns soluble in 4 parts of water but insoluble in alcohol or ether; it has a sweetish taste and melts and decomposes at 230°.

The fact that the amino-group cannot be expelled by hydrolysis establishes the structure of glycocoll. It behaves as both acid and base, forming salts with acids and also with bases. Its copper salt separates in large, dark blue needles on dissolving cupric oxide in hot glycocoll solution: $(C_2H_4O_2N)_2Cu + H_2O$. With ferric chloride it gives an intense red coloration. When heated with baryta, it loses CO_2, forming methylamine; with nitrous acid it gives glycollic acid.

Various *alkyl* and other derivatives have been obtained synthetically from glycocoll:

$$\begin{array}{l} CH_2\cdot NH\cdot COCH_3 \\ | \\ COOH \end{array} ; \quad \begin{array}{l} CH_2\cdot NH\cdot CH_3 \\ | \\ COOH \end{array} ; \quad \begin{array}{l} CH_2—N(CH_3)_3 \\ | \qquad\quad | \\ CO——O \end{array}$$

Aceturic acid; Sarcosine (derived from caffeine and from creatine); Betaine (from the beet)

With nitrous acid, the esters of glycocoll yield ETHYL DIAZOACETATE,

$$NH_2\cdot CH_2\cdot COO\cdot C_2H_5 + HNO_2 = 2H_2O + \begin{array}{c} N \\ \| \\ N \end{array}\!\!>\! CH\cdot COOC_2H_5,$$

which is a yellow oil boiling at 141° and readily decomposes and reacts with evolution of nitrogen; it serves for the synthesis of pyrazole.

LACTIC ACIDS, $OH\cdot C_2H_4\cdot CO_2H$

The two structural isomerides foreseen by theory are known: α- and β-hydroxypropionic acids. Also the α-acid exists in two stereoisomeric forms (l = lævo- and d = dextro-rotatory) owing to the presence of an asymmetric carbon atom (p. 18) and in an inactive form (i = inactive), consisting of a mixture in equal proportions of the two stereoisomerides These lactic acids form *anhydrides* similar to those of glycollic acid (*see above*).

The lactic acids give Uffelman's *reaction*, that is, they cause the amethyst-coloured solution obtained on adding a drop of ferric chloride to a dilute salicylic acid solution to turn yellow; this reaction is also given by citric, oxalic, and the tartaric acids.

(1) *i*-ETHYLIDENELACTIC ACID ($l + d$) (2-Propanoloic or α-Hydroxypropionic Acid or Ordinary Lactic Acid of Fermentation), $CH_3\cdot CH(OH)\cdot COOH$, is found in milk rendered acid by the action of the *lactic acid bacillus* (*see* Fig. 114, p. 122), in milk-sugar (also cane- and grape-sugars, gum, starch, &c.) which undergoes acid fermentation (*lactic fermentation*) even in absence of air, although oxygen facilitates the change. Cabbage fermented with vinegar and salt (Sauerkraut), gastric juice, putrefied cheese, fresh fodder siloed, and fermented muscular juices and the brain[1] also contain free lactic acid.

When pure it melts at 18° and boils at 120° under 12 mm. pressure, but usually it forms a dense syrup soluble in water, alcohol, or ether. It is optically inactive, as it consists of a *racemic* mixture of dextro- and lævo-acids (*see* pp. 19 and 20). The two modifications can be separated by crystallisation

[1] It appears now to be proved that the lactic acid in the human organism is formed in proportion to the muscular and cerebral work, and, together with carbon dioxide, which is also a waste product of the cells of the organism during wakefulness, produces *sleep*. While we sleep, the blood carries off these waste products more easily, the cells then recovering their function and their sensibility. The connection between sleep and fatigue is well known and is shown not only by the fact that after great muscular or cerebral fatigue sleep is more profound, but by the results of the following experiment: if the blood of a very tired dog is injected into the veins of another dog in a normal state, this dog soon exhibits signs of great fatigue and goes to sleep; these results are not observed if the blood injected is that of a non-fatigued dog. During heavy muscular labour, the air expired contains more CO_2 than in a state of repose and more still than during sleep. The carbon dioxide diminishes the oxygen so much needed by the muscles and brain, so that the activity of these remains depressed. As is well known, lactic acid has a depressing action on the nervous cells, injection of the acid into the veins of any person inducing symptoms of fatigue and sleepiness and finally sleep. The continuance of sleep is due to the fact that the blood flows more slowly to the brain, to which it hence carries less oxygen. It appears, indeed, to be proved that in general five or six hours' sleep—very deep for two hours—is sufficient for the blood to wash away these waste products of active cellular work and to restore activity to all the cerebral centres.

of the strychnine salts or by cultivating in the solution *Penicillium glaucum*, which first destroys the lævo-acid (*see* p. 22). When heated, the active acid is transformed, to the extent of one-half, into the optical enantiomorph, so that the inactive racemic acid is obtained. If kept in a desiccator, it is partly converted into anhydride owing to loss of water. When distilled under reduced pressure, it yields water, carbon dioxide and lactide (*see above*). If heated with dilute sulphuric acid it decomposes, like many other α-hydroxy-acids, into acetaldehyde and formic acid.

PREPARATION. Various processes have been tried for the preparation of lactic acid. For instance, 3 kilos of cane-sugar and 15 grms. of tartaric acid are dissolved in 13 litres of boiling water. In a few days' time, after the cane-sugar has been converted into glucose and levulose, 4 litres of acid milk and 100 grms. of putrefied cheese (also 1·5 kilo of zinc carbonate to fix the lactic acid, which otherwise would arrest the lactic fermentation) are added and the mixture left for a week at a temperature of 40° to 45°, by which means the maximum production of lactic acid is obtained. The acid separates as zinc lactate in crystalline crusts which, after purification (by recrystallisation), are suspended in water and decomposed with H_2S in order to remove the zinc as insoluble sulphide. The filtered liquid is concentrated to a syrupy consistency and then extracted with ether, which does not dissolve the impurities (zinc salts, mannitol, &c.); on evaporation of the ether, pure syrupy lactic acid is obtained.[1] Besides the decomposition of the sugar, various secondary reactions always accompany lactic fermentation, and the yield of the acid is scarcely 20 per cent. of the weight of the sugar taken.

A better yield is, however, obtained by Larrieu's process (Fr. Pat. 206,506), which consists in treating, say, 900 kilos of starch with 100 kilos of malt and with hot water to bring the temperature to 50°, this being finally raised to 75°, the mass being continually stirred. Half a kilo of ammonium nitrate is next added to the vat and then the lactic ferment, the temperature being maintained at 50° to 60° for 20 to 30 days, and the acid formed being gradually half saturated with soda. The mass is ultimately filtered and the liquid concentrated to a sp. gr, of 1·21 (25° Bé.), mixed with 500 kilos of powdered calcium carbonate and filtered. The solution of calcium lactate is decomposed with the calculated quantity of sulphuric acid, the calcium sulphate being removed by filtration and the aqueous lactic acid evaporated to a syrupy consistency.

Jacquemin prepares the acid from worts similar to those employed in breweries (barley mashed at 50° with malt, then boiled to destroy the diastase and cooled to 45°) by the addition of pure lactic ferment and calcium carbonate. After 5 to 6 days, the mash is filtered and concentrated, the calcium lactate being then decomposed in the usual way with sulphuric acid.

Dreher works in a similar manner, but with glucose solutions containing 1 per cent. of nutrient substances for the ferment (*e.g.* sodium phosphate, nitre, salt, &c.).

Industrially, however, lactic acid is now always obtained from milk residues (*whey* or *molasses* of milk-sugar, which remain after the removal of the butter from the milk in the separator; also cheese by coagulation with rennet in the hot). The whey is concentrated in open vessels or, better, in vacuum pans, to 16° Bé., and is then introduced into wooden vessels in which, at a temperature of 40°, the lactic ferment is added in the form either of part of the liquid from a previous fermentation or of putrefied cheese. Powdered chalk is added to neutralise the acid formed, the liquid being stirred from time to time and the fermentation allowed to continue for 10 to 12 days. After decantation, the calcium lactate is decomposed with dilute sulphuric acid, the liquid mass being well mixed. In some cases, before the calcium lactate is decomposed, it is separated by concentrating the solution, and is recrystallised from a little hot water, which should dissolve 20 per cent. of it. The calcium sulphate formed is removed by passing the mass through

[1] Kiliani treats 500 grms. of inverted sugar with 250 grms. of water and 15 grms. of sulphuric acid at 50° to 60° for 2 hours, and then adds gradually 400 c.c. of concentrated caustic soda solution (1 : 1), the liquid being kept boiling meanwhile.

The soda is subsequently neutralised with 50 per cent. sulphuric acid and the solution left for 24 hours to deposit crystalline sodium sulphate. The lactic acid is extracted with alcohol—which does not dissolve the sulphate—the alcohol being recovered by distillation. The crude lactic acid remaining is diluted, saturated with zinc carbonate and evaporated; the zinc lactate is then allowed to separate and is filtered off, redissolved in hot water and decomposed with H_2S. After filtration, the liquid is concentrated *in vacuo*, pure lactic acid being thus obtained.

a filter-press (*see* figure in the section on Sugar) and the clear lactic acid solution concentrated in a double- or triple-effect apparatus until it attains a concentration of 50 per cent. The further small quantity of gypsum which is then deposited is separated by filtration, the resulting yellowish brown liquid representing commercial, crude, 50 per cent. (by weight) lactic acid. This should not contain more than 1·5 per cent. of ash, and should not contain sulphate or reduce Fehling's solution.

The lactic acid prepared from the molasses of milk-sugar factories is more impure than the above.

According to a patent filed in 1905. lactic acid is also obtained from a mixture of bran and barley, and an English patent (No. 26,415, 1907) describes the preparation of pure, concentrated lactic acid by the distillation of the commercial 50 per cent. acid in a rapid current of air or of an indifferent gas.

Very *pure* lactic acid is obtained by extracting the crude product with amyl alcohol—which does not dissolve the impurities (sugar, gum, mineral substances)—and distilling *in vacuo*. The *impurities* are estimated by titrating the acid with normal caustic potash solution in presence of phenolphthalein.

USES AND PRICE. Until a few years ago the uses of lactic acid were limited to the preparation of soluble lactates for medicinal purposes, but its manufacture has recently been considerably extended owing to its employment in the dyeing of wool, silk, &c., in place of tartaric acid, tartar and oxalic acid, for the reduction of the chromium compounds with which wool to be treated with fast dyes (alizarin dyes, &c.) is mordanted. For the same reasons it is advantageously employed in the chrome tanning of skins, its value in this case being sometimes regarded as due to its ability to keep calcium salts in solution and thus prevent the formation of certain harmful deposits. The crude 50 per cent. acid is most commonly sold, and it is necessary to ascertain whether by 50 per cent. is meant 50 kilos per 100 litres or per 100 kilos of solution ; in the former case the strength of the acid is only 43 per cent. by weight (*i e.* 100 kilos contain 43 kilos of acid).

Commercial, brown, 50 per cent. lactic acid costs about 64*s.* per quintal ; the paler, yellow product of the same strength, 105*s.* ; the pure (sp. gr. 1·21), 3*s.* 7*d.* per kilo, and the chemically pure 12*s.* per kilo. Italy imported the following quantities of pure lactic acid at 104*s.* per quintal : 996 quintals in 1907 ; 650 in 1908 ; 520 in 1909 ; and 490 in 1910, when the amount exported was 51 quintals. The import duty in Italy is 12*s.* per quintal.

Salts of Lactic Acid are generally soluble to some extent in water. *Calcium lactate*, $(C_3H_5O_3)_2Ca + 5H_2O$, forms mammillary aggregates of white needles soluble in 9·5 parts of cold water, and in all proportions in hot water ; it is insoluble in cold alcohol. The water of crystallisation is evolved in a vacuum desiccator or on heating to 100°. At 250° it loses H_2O, giving *calcium dilactate*, which is less soluble in alcohol than the original salt. *Zinc lactate* and *ferrous lactate* crystallise with $3H_2O$, the latter in yellowish crystals ; both are used in medicine.

ALANINE, $CH_3 \cdot CH(NH_2) \cdot COOH$, is obtained from the corresponding aldehyde-ammonia by the action of hydrocyanic acid. From the inactive, synthetical compound, the active stereoisomerides are separated by means of the strychnine or brucine salts. The action of PCl_5 expels both the hydroxyl- and the amino-groups, giving *lactyl* chloride, $CH_3 \cdot CHCl \cdot COCl$; which gives α-chlorpropionic acid, $CH_3 \cdot CHCl \cdot COOH$, when treated with water.

(2) *d*-ETHYLIDENELACTIC ACID (Paralactic or Sarcolactic Acid) differs from ordinary lactic acid only in the greater solubility of its zinc salt ($+ 2H_2O$), and the less solubility of its calcium salt ($+ 4H_2O$). It is found in Liebig's extract of meat, and it is contained in the muscular juices, and is also formed in certain lactic fermentations.

(3) *l*-ETHYLIDENELACTIC ACID is formed during the fermentation of aqueous cane-sugar solutions by *Bacillus acidi lævolactici*.

(4) ETHYLENELACTIC ACID (Hydracrylic, β-Hydroxypropionic or 3-Propanoloic Acid), $OH \cdot CH_2 \cdot CH_2 \cdot COOH$, differs from its isomerides in that, when heated, it loses a molecule of water, giving, not the anhydride, but acrylic acid, $CH_2 : CH \cdot CO_2H$. Further, with oxidising agents it gives, not acetic acid, but oxalic acid and carbon dioxide. It contains no asymmetric carbon atom and is hence optically inactive. It can be prepared synthetically from (1) β-iodopropionic acid, or (2) ethylene, $CH_2 : CH_2$, by addition of hypochlorous acid, giving $OH \cdot CH_2 \cdot CH_2Cl$, which is then converted into the nitrile

$OH \cdot CH_2 \cdot CH_2 \cdot CN$, hydrolysis of the latter giving ethylenelactic acid. The acid is a colourless, syrupy liquid and forms a calcium salt ($+ 2H_2O$) and a readily soluble zinc salt ($+ 4H_2O$).

HYDROXYBUTYRIC ACIDS, $OH \cdot C_3H_6 \cdot CO_2H$

Five isomerides are theoretically possible, four being known: two *α-acids*, one *β-acid*, and one *γ-acid* (prepared only as salts).

α-HYDROXYBUTYRIC ACID, $CH_3 \cdot CH_2\ CH(OH)\ CO_2H$, melts at 43° and is synthesised as the inactive, racemic form, which can be resolved into its active components by means of brucine (*see* p. 22).

α-HYDROXYISOBUTYRIC ACID (Acetonic or 2-Methyl-2-propanoloic Acid), $OH \cdot C(CH_3)_2 \cdot CO_2H$, melts at 79°, boils at 212°, and is obtainable by various synthetical methods from dimethylacetic acid, acetocyanohydrin, α-aminobutyric acid, &c.

β-HYDROXYBUTYRIC ACID, $CH_3\ CH(OH) \cdot CH_2\ CO_2H$, is obtained by oxidising aldol or reducing acetoacetic acid, these methods of formation indicating its constitution. It forms a syrup and its lævo-isomeride is found in the blood and in diabetic urine.

HIGHER HYDROXY-ACIDS

α-HYDROXYVALERIC ACID, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH(OH)\ CO_2H$, melts at 29°.

α-HYDROXYISOVALERIC ACID, $(CH_3)_2CH \cdot CH(OH) \cdot CO_2H$, melts at 86°.

METHYLETHYLGLYCOLLIC ACID, $\begin{matrix} CH_3 \\ C_2H_5 \end{matrix}\!>\!C\!<\!\begin{matrix} OH \\ CO_2H \end{matrix}$, melts at 68°.

α-HYDROXYCAPROIC ACID (Leucinic Acid), $CH_3 \cdot [CH_2]_3 \cdot CH(OH) \cdot CO_2H$, melts at 73° and is obtained from leucine (*see later*).

α-HYDROXYMYRISTIC ACID, $CH_3 \cdot [CH_2]_{11} \cdot CH(OH) \cdot CO_2H$, melts at 51°.

α-HYDROXYPALMITIC ACID, $CH_3 \cdot [CH_2]_{13} \cdot CH(OH) \cdot CO_2H$, melts at 82°.

α-HYDROXYSTEARIC ACID, $CH_3 \cdot [CH_2]_{15}\ CH(OH) \cdot CO_2H$, melts at 84° to 86°, and is formed by the action of cold concentrated sulphuric acid on oleic acid, this method being sometimes used practically to prepare solid fatty acids from liquid oleic acid (*see* section on Fats).

The Sulphuric Ether of α-Hydroxystearic Acid, $C_{18}H_{35}O_2(OSO_3H)$, is used in the dyeing of cotton with Turkey-red (*see below*).

Various other β-hydroxystearic and dihydroxystearic acids, with melting-points higher than those of the liquid fatty acids which yield them, are also known.

B. MONOBASIC UNSATURATED HYDROXY-ACIDS

The α-Hydroxyolefinecarboxylic Acids are prepared by hydrolysing, with HCl in the cold, the nitriles obtained by the addition of hydrogen cyanide to olefinic aldehydes. If the double linking (Δ) is in the βγ-position, these hydroxy-acids are converted into γ-ketocarboxylic acids when boiled with dilute HCl; thus, α-hydroxypentenoic acid, $CH_3 \cdot CH : CH \cdot CH(OH) \cdot CO_2H$, yields levulinic acid, $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H$.

Several β-Hydroxyolefinecarboxylic Acids are known. The most simple is *β-hydroxyacrylic* or *formylacetic acid*, $CO_2H \cdot CH : CH \cdot OH$, which, like the others, readily forms esters and halogen derivatives.

γ- and δ-Hydroxyolefinecarboxylic Acids are known mostly in the form of *lactones* (*see* pp. 295 and 322).

RICINOLEIC ACID (Hydroxyoleic Acid), $C_{18}H_{34}O_3$, or $CH_3 \cdot [CH_2]_5 \cdot CH(OH)\ CH_2 \cdot CH : CH \cdot [CH_2]_7 \cdot CO_2H$, constitutes, in the form of glyceride, the greater proportion of castor oil, and, on dry distillation under reduced pressure, decomposes into œnanthaldehyde, $C_7H_{14}O$, and undecylenic acid, $C_{11}H_{20}O_2$. It solidifies at $-6°$ and melts at $+4°$. It forms lead and barium salts soluble in ether, and, when fused with KOH, yields sebacic acid, $C_8H_{16}(CO_2H)_2$, and sec. octyl alcohol. It forms a solid bromide and an oily ozonide (by the addition of ozone) which decomposes, giving, among other products, a large proportion of azelaic acid (Molinari and Caldana, 1909), the position of the double linking—established by Goldsobel (1894) by means of ricinostearolic acid—being thus confirmed. By nitrous acid it is transformed into the isomeric *ricinelaidinic acid,* melting at 53°. By decomposing the ozonide of methyl ricinoleate, Haller and Brochet (1910)

obtained β-*hydroxypelargonic acid*, $CH_3 \cdot [CH_2]_5 \cdot CH(OH) \cdot CO_2H$, azelaic acid and the corresponding semi-aldehyde.[1]

By treating castor oil slowly with cold, concentrated sulphuric acid, *ricinosulphuric acid* is obtained, this being the most important constituent of Turkey-red oil, which is used in large quantities in the dyeing and printing of cotton textiles with alizarin red (*Adrianople red*).[2] It is also used for greasing wool to be spun and for dressing textiles.

The treatment of castor oil with concentrated sulphuric acid yields ricinoleic acid more or less polymerised or condensed into anhydrides, glycerolsulphuric esters of ricinoleic acid and a preponderating proportion of ricinosulphuric acid, which is an ester of sulphuric acid soluble in water: $C_{18}H_{33}O_2 \cdot OH + H_2SO_4 = H_2O + C_{18}H_{33}O_2 \cdot O \cdot SO_3H$. This acid

[1] Ricinoleic Acid was prepared pure by Krafft (1888) by hydrolysing castor oil, the fatty acids thus obtained being cooled at 0° and the solid acids separated by squeezing (at 10°). The dry lead or barium salt was then prepared and extracted with ether, which leaves undissolved the last traces of the salts of the solid fatty acids; the salt of ricinoleic acid is dissolved and gives the pure acid.

With concentrated sulphuric acid, the acid gives (Benedikt and Ulzer, 1887; Juillard, 1894 and 1895; Chonowsky, 1909, and especially Ad. Grün, 1906 and 1909) *ricinoleinsulphonic acid*, $C_{17}H_{32}(O \cdot SO_3H) \cdot CO_2H$; by hot water this acid is hydrolysed with separation of sulphuric acid and formation of a condensed ester (*ricinoleinricinoleic ester*), $C_{17}H_{32}(OH) \cdot CO \cdot O \cdot C_{17}H_{32} \cdot CO_2H$, the condensation taking place between the carboxyl group of one molecule and the hydroxyl of another; only one acetyl group is introduced into the molecule of this compound by the action of acetic anhydride. Various isomeric condensed anhydrides of dihydroxystearic acids are also easily prepared: these are solid and have the constitution $C_{17}H_{33}(OH)_2.CO.O.C_{17}H_{33}(OH).CO_2H$ (4 isomerides) and can be converted into the corresponding *dihydroxystearic acids*. One of the latter melts at 90° and is optically active ($[\alpha]_D = + 6 \cdot 45°$), two melt at 69·5° and 108° respectively and are inactive, while the fourth melts at 126° and is active; the positions of the two hydroxyl groups seem to be 9 and 12, or 10 and 12 (for those with the higher melting-points).

The action of sulphuric acid on *olive oil* partly decomposes the triolein into glycerol and oleic acid and partly transforms it only into diolein. To some extent the double linking of oleic acid fixes H_2O and forms hydroxystearic acid, which is partly converted into the *sulphuric ester of* 1 : 10-*dihydroxystearic acid*. Besides free ricinoleic acid, undecomposed glycerides and glycerol, Turkey-red oil contains (according to Juillard), the sulphuric ester of ricinoleic acid, dihydroxystearic acid and the two corresponding mono- and di-sulphuric esters, as well as diricinoleic acid and other polymerides (up to *pentaricinoleic acid*).

The phenomenon of polymerisation is, indeed, of great importance as regards the effects produced in practice by the sulphoricinate.

[2] Turkey-Red Oil (or *sulphoricinate*) is prepared by treating castor oil—in an open, double-bottomed, iron vessel furnished with a stirrer—with 20 per cent. (in summer) or 25 per cent. (in winter) of concentrated sulphuric acid (66° Bé.), which is added very slowly during 5 or even 8 hours, so that the temperature of the mass never exceeds 35°; if these precautions are neglected, SO_2 is evolved. When necessary, the temperature is moderated by passing cold water through the jacket. The mixture is left for some hours until a small portion is found to be soluble in water. The mass is then discharged into a wooden vat containing a quantity of sodium chloride or sulphate equal to that of the oil treated. After mixing, the liquid is allowed to stand for some hours, the excess of acid (10 to 12 per cent. is fixed in the sulphoricinate) being next removed by decanting the aqueous portion and washing the remainder in the same manner and afterwards with two successive quantities of water half saturated with common salt; sufficient concentrated ammonia or sodium hydroxide solution is then added to give a neutral (or amphoteric) reaction. The quantity and concentration of the alkali to be added are determined by a preliminary test on a small portion, which gives also the content in fatty acids of the commercial ricinate. It is usually a clear, yellowish solution, which gives a clear solution when diluted with 2 to 4 vols. of water and a milky emulsion when mixed with 5 to 6 vols of water or with dilute alkali.

The commonest strengths are 40, 50, and 60 per cent. of *total fat* (liberated from the alkali), which is estimated by Herbig's method (1906); 10 grms. of the sulphoricinate are dissolved in 50 c.c. of hot water, 25 c.c. of dilute HCl being then added and the solution boiled for 4 or 5 minutes, during which time it is kept stirred to avoid spurting. It is next cooled (and, if desired, the *volume* of the washed fatty acids can be measured in a burette) and extracted in a separating funnel with 200 c.c. of ether, which is washed with three separate quantities of 15 to 20 c.c. of water. The ether is distilled off from a tared flask, the fat being heated over a naked flame and shaken for a couple of minutes, dried at 105° for half an hour and weighed. When neutral, not sulphonated, fats are present, they are determined by treating 30 grms. of the sulphoricinate with 50 c.c. of water, 20 c.c. of ammonia, and 30 c.c. of glycerol, the whole being extracted with ether, which is washed with water and evaporated in a tared dish. To ascertain if the sulphoricinate is the ammonium or sodium compound, tests are made for these bases in the wash-water separated in estimating the total fat; the ammonia is estimated by heating with excess of alkali and collecting the ammonia in a standard solution of sulphuric acid, while the soda is determined by evaporating to dryness, calcining the residue and weighing as sodium sulphate.

If the sulphoricinate were not prepared from castor oil (inferior products are obtained from olive oil with a larger amount of sulphuric acid), it will give a turbid solution in alcohol, while the *acetyl number* (*see* p. 189) of the *total fat* is only 5 to 10 (for olive oil), that of true sulphoricinate being usually 140 and always above 125. Further, the iodine number of the acids of true sulphoricinate is never lower than 68 to 70, whilst with other oils it is decidedly lower than 70. In the Zeiss oleorefractometer the fatty acids of pure sulphoricinate give a reading of 74.

The complete analysis of a good sulphoricinate gave 58 per cent. of total fat (composed of 47 per cent. of insoluble fatty acids, 1·5 per cent. of neutral fats and 9·5 per cent. of fatty sulpho-acids soluble in water), 1·8 per cent. of ammonia, and 4·6 per cent. of sulphuric acid. In true sulphoricinates, however, the ratio of sulphuric to sulphoricinic acid should not be 4·6 : 9·5, but rather 4·6 : 22, and the sulphuric acid as sodium or ammonium sulphate should not exceed 0·2 to 0·3 per cent. The soluble sulpho-acids are estimated by treating 10 grms. of the total fatty acids with (not more than) 10 c.c. of ether and 30 c.c. of saturated sodium chloride solution free from sulphates; the mixture is shaken and filtered through a moist filter, the sulpho-acids in the filtrate being precipitated with barium chloride.

The price of Turkey-red oil is based on its content of total fat and is usually about 10*d.* per unit of fat per 100 kilos of sulphoricinate. This content is often determined in a graduated burette, by decomposing a given quantity of the sulphoricinate with sulphuric acid, diluting with water and measuring, in the burette, the fat which rises to the surface after some hours.

is separated from water by addition of salt or dilute mineral acid in the cold; it is only slightly soluble in ether, and its calcium, lead, &c., salts are insoluble in water. Ricinosulphuric acid is not decomposed in the hot by water or dilute alkali, but it decomposes readily into sulphuric and ricinoleic acids when boiled with dilute hydrochloric or sulphuric acid. By using an excess of concentrated sulphuric acid, Grün (1907) obtained 9 : 12-dihydroxystearic acid. Ricinosulphuric acid or its sodium or ammonium salt is of importance in Turkey-red oil, since, when the latter is diluted with water, it serves to keep in a state of solution the castor oil or other unaltered oil always found in greater or larger quantity in Turkey-red oil.

Treatment of olive oil or oleic acid with sulphuric acid yields hydroxystearosulphuric acid, which is *saturated*, $C_{18}H_{34}O_2$ (oleic acid) + H_2SO_4 = $C_{18}H_{35}O_2\ O \cdot SO_3H$; so that the iodine number may be used to distinguish true sulphoricinates from saturated ones, which are unable to undergo those characteristic oxidations necessary to dyeing operations. With an excess of sulphuric acid, hydroxystearosulphuric acid takes up a molecule of water, yielding sulphuric acid and hydroxystearic acid (saturated), $C_{18}H_{35}O_2 \cdot OH$.

C. POLYVALENT MONOBASIC HYDROXY-ACIDS

These are derived from polyhydric alcohols by the oxidation of one primary alcoholic group to carboxyl, the other two or more alcoholic groups remaining unaltered; they exhibit behaviour analogous to that of lactic acid. The number of the hydroxyls is deduced from the acetyl number (*see* p. 189). These acids, which are gelatinous and crystallise with difficulty, are sometimes obtained by the gradual oxidation of saccharine substances or of unsaturated acids.

GLYCERIC ACID ($\alpha\beta$-**Dihydroxypropionic** or **Propandioloic Acid**), $OH \cdot CH_2\ CH(OH) \cdot CO_2H$, obtained by oxidising glycerol with nitric acid, exists in optically active forms,[1] and is soluble in alcohol, water, or acetone (which does not dissolve glycerol).[2] As has already been mentioned, *dihydroxystearic acid*, $C_{18}H_{34}O_2(OH)_2$, is formed by oxidising oleic acid.

ERYTHRIC ACID (**Butantrioloic Acid**), $OH \cdot CH_2 \cdot [CH(OH)]_2 \cdot CO_2H$, is formed on gentle oxidation of fructose or erythritol and is monobasic and tetravalent.

Of the pentavalent monobasic acids, four pentonic or *pentantetroloic* isomerides, $C_4H_5(OH)_4 \cdot CO_2H$, are known, namely, **arabonic acid** (by oxidising arabinose), and *ribonic*, *xylonic*, and *lyxonic acids*.

Saccharinic or **hexantetroloic acid**, $C_5H_7(OH)_4 \cdot CO_2H$, is obtained by treating glucose or fructose with lime, while *iso-* and *meta-saccharinic acids* are also known as salts, which are readily obtained from the lactones.

The **hexonic acids** or **hexanpentoloic acids**, $C_5H_6(OH)_5 \cdot CO_2H$, are known in some cases only as lactones and are obtained by reduction of the corresponding dibasic acids (saccharic acid, &c.) or by gentle oxidation (with bromine water) of the corresponding sugars (hexoses), to which they are closely related:

Mannose, $C_6H_{12}O_6$,	yields	*mannonic*	*acid*,	$C_6H_{12}O_7$.
Galactose	„	*galactonic*	„	„
Glucose	„	*gluconic*	„	„
Gulose	„	*gulonic*	„	„
Idose	„	*idonic*	„	„
Talose	„	*talonic*	„	„

These acids can be obtained synthetically by hydrolysing the nitriles (*see* pp. 265 and 268) of the simpler sugars (pentoses).

[1] From the racemic form, the lævo-modification can be obtained by fermenting the ammonium salt with *Penicillium glaucum*, and the dextro-form by the direct action of *Bacillus ethaceticus*.

[2] It forms a calcium salt, $(C_3H_5O_4)_2Ca + 2H_2O$, soluble in water, whilst the lead salt is only slightly soluble in cold water. Among the derivatives of this acid are *serine*, $OH \cdot CH_2\ CH(NH_2) \cdot CO_2H$, which, being an amino-derivative, has a neutral reaction and forms salts with both acids and bases; it is obtained by boiling silk-gum with dilute sulphuric acid and is soluble in water but insoluble in alcohol or ether

Among the higher derivatives are (1) ornithine (*$\alpha\delta$-diaminovaleric acid*), $NH_2 \cdot CH_2\ CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$, which is formed on decomposition of *arginine*, contained in germinating lupins, and (2) lysine, or *$\alpha\epsilon$-diaminocaproic acid*, $NH_2 \cdot [CH_2]_4 \cdot CH(NH_2) \cdot CO_2H$, which is obtained on decomposing casein or glue with hydrochloric acid.

Further, the hexonic acids yield the sugars on reduction, or the dibasic acids on oxidation with nitric acid.

These acids can be separated one from another by the phenylhydrazine reaction; all of them have the same constitution, but they differ in the spatial arrangement of the groups composing the molecule, since they are stereoisomerides containing various asymmetric carbon atoms:

$$OH \cdot CH_2\ CH(OH) \cdot CH(OH) \cdot CH(OH)\ CH(OH) \cdot CO_2H,$$

and for each of these acids, except talonic, the dextro- (*d*), lævo- (*l*), and inactive (*i*) forms are known.

Some of these stereoisomeric forms are transformed into others simply by the action of pyridine and a little water (*e.g.* *d*-mannonic acid gives *d*-gluconic acid and *vice versa*), and the inactive forms are resolved into their active constituents by means of the strychnine salts (*see* p. 22).

The **HEPTONIC ACIDS** are also derived from the corresponding sugars, the heptoses (*see later*), *e.g.* *rhamnohexonic acid*, $C_6H_8(OH)_5 \cdot CO_2H$, from rhamnose, *glucoheptonic acid*, $C_6H_7(OH)_6\ CO_2H$, &c.

D. MONOBASIC ALDEHYDIC ACIDS

(and Aldehydic Alcohols and Dialdehydes)

GLYOXYLIC or **ETHANOLOIC ACID, $CO_2H \cdot CHO + H_2O$,** gives up the molecule of water with which it is combined without decomposing, and may be regarded as having a structure similar to that of chloral hydrate, $CO_2H \cdot CH(OH)_2$; the salts also correspond with this formula, although they retain the aldehydic character. It occurs widespread in nature in sour fruit (gooseberries, &c.), and is obtained synthetically by heating dibromoacetic acid, $CO_2H \cdot CHBr_2$, with water, by reducing oxalic acid electrolytically, or by oxidising ethyl alcohol with nitric acid. It crystallises with difficulty, dissolves in water and distils in steam.

FORMYLACETIC ACID (Semi-aldehyde of Malonic Acid), **$CO_2H \cdot CH_2 \cdot CHO$,** is obtained as acetal from the acetal of acrolein. The isomeric **β-hydroxyacrylic acid** (*hydroxymethyleneacetic acid*), $CO_2H \cdot CH : CH \cdot OH$, is also known and is obtained as ester by a synthesis similar to that of ethyl acetoacetate (*see* p. 332). It condenses readily to *trimesic acid*, $C_6H_3(CO_2H)_3$.

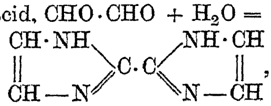
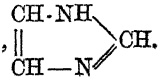
GLYCURONIC ACID, $CO_2H \cdot [CH(OH)]_4 \cdot CHO$, is obtained by reducing saccharic acid, and, as lactone, melts at 175°.

GLYCOLLIC ALDEHYDE (Ethanolal), **$OH \cdot CH_2 \cdot CHO$,** is obtained by the action of baryta water on bromoacetaldehyde in the cold. It is known only in aqueous solution and may be regarded as the simplest member of the sugar group, of which it gives all the reactions; it reduces Fehling's solution, even in the cold. When oxidised with bromine water it gives glycollic acid, whilst in presence of dilute alkali it condenses, forming tetrose. If heated in a vacuum, it condenses to a syrup, which retains the reducing character. With phenylhydrazine acetate it yields glyoxal phenylosazone.

GLYCERALDEHYDE, $OH \cdot CH_2 \cdot CH(OH) \cdot CHO$, is obtained together with dihydroxyacetone (as *glycerose*) by oxidising lead glycerate with bromine, or by hydrolysis of its acetal. On condensation, it gives acrose.

ALDOL, $CH_3 \cdot CH(OH) \cdot CH_2 \cdot CHO$ (*see* p. 205), which belongs to this group of compounds, forms a dense oil soluble in water.

GLYOXAL (Ethandial), **$CHO \cdot CHO$,** is the dialdehyde of glycol, and hence combines with 2 mols. of bisulphite $[C_2H_2O_2(SO_3HNa)_2 + H_2O]$ or hydrocyanic acid. It is formed, together with glycollic acid, by gentle oxidation of acetaldehyde with nitric acid. It forms a white mass which is soluble in alcohol or ether and absorbs water with avidity. Even in the cold, alkalis transform it into glycollic acid, $CHO \cdot CHO + H_2O = OH \cdot CH_2 \cdot CO_2H$.

With concentrated ammonia, it gives *glycosine*, , which is converted to a large extent into *glyoxaline* (*iminazole*), 

E. MONOBASIC KETONIC ACIDS

(and Keto-alcohols, Diketones and Keto-aldehydes)

Ketonic acids show all the general reactions of acids—*i e.* of the carboxyl group (p. 266)—and of ketones—*i.e.* of the carbonyl group, CO (p. 204). Their constitution can be deduced from the various syntheses and from the known constitution of the hydroxy-acids derived from them on reduction.

Interesting behaviour is shown by the esters of the *β-ketonic acids*. which, owing to the mobility of a hydrogen atom adjacent to the carbonyl, reacts sometimes in the ketonic form and sometimes in the isomeric *enolic* form, which represents an unsaturated, tertiary alcohol:

$$\underset{\text{Ethyl acetoacetate (keto-form)}}{CH_3\cdot CO\cdot CH_2\cdot CO_2C_2H_5} \rightleftarrows \underset{\text{Ethyl hydroxycrotonate (enol-form)}}{CH_3\cdot C(OH):CH\cdot CO_2C_2H_5.}$$

The enolic form is stable only as derivatives, *e.g.* the acetyl-derivatives, $CH_3\cdot C(O\cdot CO\cdot CH_3):CH\cdot CO_2C_2H_5$, these derivatives being the more stable, the more negative the residues introduced in the direction of the carboxyl.

This phenomenon is *tautomerism* or *pseudoisomerism* (*see* p. 17).

If the *α*-carbon atom, adjacent to the carbonyl, has one of its hydrogen atoms replaced by an alkyl group, thus, $CH_3\cdot CO\cdot CHR\cdot CO_2C_2H_5$, the phenomenon of tautomerism is still observed, but this ceases to be the case when both these hydrogen atoms are replaced, as in $CH_3\cdot CO\cdot CR_2\cdot CO_2C_2H_5$. The mobile hydrogen causing the tautomerism is solely that situate between two carbonyls (1 : 3 diketones):

$$—CO—CH_2—CO— \leftrightarrows —C(OH):CH\cdot CO—$$

so that such behaviour is not shown by acetylformic acid, $CH_3\cdot CO\cdot CO_2H$; diacetyl, $CH_3\cdot CO\cdot CO\cdot CH_3$; acetonylacetone, $CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3$; levulinic acid, $CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H$, &c.

The tautomeric forms can be distinguished and are stable in the crystalline state, even near the melting-point; the reciprocal transformation is continuous and very rapid in either the fused or dissolved state, the two forms finally attaining proportions varying with the conditions (especially temperature and nature of solvent). If separation of the two forms by means of a reagent is attempted, the equilibrium is displaced and the second tautomeric form is transformed into the one which has reacted, so that the mixture behaves as a single substance, unless two reagents are used which act with equal velocities on the two forms giving different, separable compounds; syntheses with ethyl chlorocarbonate appear to correspond with these conditions, which are, however, not easy to obtain.

When separated, the two forms can be readily distinguished, since the enol gives an intense coloration with ferric chloride, with which the ketone does not react. After some days, however, the coloration yielded by the former becomes paler, while a colour also appears in the mixture of ketone and ferric chloride, a condition of equilibrium between the two forms being slowly arrived at in each case. Sometimes the enolic form remains unchanged for a long time in chloroform solution, although when dissolved in alcohol it is transformed more or less completely into the ketonic form in the course of a few days.

The enolic form—which is soluble in alkali, whereas the ketone is insoluble —*gives* (like *all compounds containing a double bond*) *a greater dispersion and refraction of light*, and also *a greater electromagnetic rotation of the plane of polarisation*,[1] than the corresponding isomerides without double bonds.

[1] Polarised light passes unchanged through a tube containing an inactive liquid, but if the tube is surrounded by a wire through which an electric current passes, the plane of polarisation is deviated, and, under equal conditions of temperature and current, the deviation is greater for a compound with a double bond than for the isomeride without such a bond.

METHODS OF PREPARATION. Ketonic acids are formed by gentle oxidation of secondary hydroxy-acids; thus, lactic acid gives pyruvic acid, $CH_3\cdot CH(OH)\cdot CO_2H + O = H_2O + CH_3\cdot CO\cdot CO_2H$.

The α-**ketonic acids** are usually obtained by hydrolysing the nitriles, this reaction indicating the constitution:

$$\underset{\text{Acetyl cyanide}}{CH_3\cdot CO\cdot CN} + 2H_2O = NH_3 + \underset{\text{Pyruvic acid}}{CH_3\cdot CO\cdot CO_2H}.$$

β-**Ketonic acids** are obtained as esters by the action of sodium or sodium ethoxide on ethyl acetate or its homologues (*see* the Ethyl Malonate Synthesis, p. 309), thus:

$$\underset{\text{Ethyl acetate}}{CH_3\cdot CO_2C_2H_5} + \underset{\text{Sodium ethoxide}}{C_2H_5\cdot ONa} = CH_3\cdot C\begin{cases}ONa\\OC_2H_5\\OC_2H_5\end{cases}$$

$$CH_3\cdot C\begin{cases}ONa\\OC_2H_5\\OC_2H_5\end{cases} + CH_3\cdot CO_2C_2H_5 =$$

$$2C_2H_5\cdot OH + \underset{\text{Ethyl sodioacetoacetate}}{CH_3\cdot C(ONa):CH\cdot CO_2C_2H_5}.$$

Acetic acid then readily expels the sodium and liberates *ethyl acetoacetate*, which has not the enolic but the ketonic constitution, $CH_3\cdot CO\cdot CH_2\cdot CO_2C_2H_5$. The total reaction is hence as follows:

$$CH_3\cdot CO_2C_2H_5 + CH_3\cdot CO_2C_2H_5 = C_2H_5\cdot OH + CH_3\cdot CO\cdot CH_2\cdot CO_2C_2H_5.$$

Similarly diketones are obtained by the interaction of ethyl acetate and simple ketones in presence of sodium ethoxide:

$$CH_3\cdot CO_2C_2H_5 + CH_3\cdot CO\cdot CH_3 = C_2H_5\cdot OH + CH_3\cdot CO\cdot CH_2\cdot CO\cdot CH_3.$$

This *ethyl acetate synthesis* has been largely used to prepare compounds of most varied characters. **Ethyl formate** acts similarly, giving hydroxymethylene derivatives [containing the group $—C(OH) =$], which are isomeric with the keto-aldehydes:

$$\underset{\text{Acetone}}{CH_3\cdot CO\cdot CH_3} + \underset{\text{Ethyl formate}}{H\cdot CO_2C_2H_5} = C_2H_5\cdot OH + \underset{\text{Hydroxymethyleneacetone}}{OH\cdot CH:CH\cdot CO\cdot CH_3}.$$

γ-**Ketonic acids** are obtained by the ketonic decomposition (*see later*) of the products of reaction of ethyl sodioacetoacetate with esters of α-halogenated acids:

$$CH_3\cdot CO\cdot CHNa\cdot CO_2C_2H_5 + R\cdot CHI\cdot CO_2C_2H_5 =$$

$$NaI + CH_3\cdot CO\cdot CH\begin{cases}CHR\cdot CO_2C_2H_5\\CO_2C_2H_5\end{cases} \longrightarrow + H_2O \longrightarrow$$

$$CO_2 + C_2H_5\cdot OH + CH_3\cdot CO\cdot \underset{\gamma}{C}H_2\cdot \underset{\beta}{C}HR\cdot \underset{\alpha}{C}O_2C_2H_5.$$

Properties of Ketonic Acids. While the α- and γ-ketonic acids are stable, the β-acids readily lose CO_2, giving the corresponding ketones. Reduction of γ-ketonic acids yields, not hydroxy-acids, but γ-lactones.

As we saw was the case with malonic acid (*see* p. 309), the esters of β-ketonic acids contain a hydrogen atom readily replaceable by metals, *e.g.* ethyl *sodioacetoacetate*, $CH_3\cdot CO\cdot CHNa\cdot CO_2C_2H_5$.

Further, ketonic acids readily form condensation products: with aniline they give quinolines; with phenylhydrazine, pyrazoles, &c.

PYRUVIC ACID, $CH_3\cdot CO\cdot CO_2H$, is obtained by the dry distillation of tartaric or racemic acid, an intermediate product in the reaction being possibly glyceric acid (formed by loss of CO_2), which then loses water and yields

pyruvic acid. It is formed also by oxidising lactic acid with permanganate or by hydrolysing acetyl cyanide. Pyruvic acid is a liquid with an odour of acetic acid and of meat-extract, and is soluble in water, alcohol, or ether. It boils at 165° and solidifies at 9°. It is a more energetic acid than propionic owing to the presence of a carbonyl group in close proximity to the carboxyl. Its constitution is indicated by the fact that with nascent hydrogen it gives ethylidenelactic acid. It readily forms condensation products (*e.g.* benzenes; and with ammonia, pyridine compounds). When heated at 150° with dilute sulphuric acid, it loses CO_2, forming acetaldehyde. Electrolysis of a concentrated solution of potassium pyruvate results in the union of the anion of the acid, $CH_3\cdot CO\cdot COO'$ with the ion OH', cyanogen and acetic acid being formed; at the same time two anions combine with loss of $2CO_2$ and formation of *diacetyl*, $CH_3\cdot CO\cdot CO\cdot CH_3$. This represents the general behaviour of potassium salts of ketonic acids on hydrolysis.

Of the derivatives, *cysteine* (α-amino-β-thiolactic acid), $SH\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$, and *cystine*, the corresponding disulphide, may be mentioned.

α-Ketobutyric acid, $CH_3\cdot CH_2\cdot CO\cdot CO_2H$, has no special importance.

ACETOACETIC ACID (β-ketobutyric acid), $CH_3\cdot CO\cdot CH_2\cdot CO_2H$, is obtained in the free state by cautious hydrolysis of its ester, and forms an extremely acid liquid soluble in water, in which it gives a red coloration with ferric chloride; when heated, it readily loses CO_2 with production of acetone.

ETHYL ACETOACETATE, $CH_3\cdot CO\cdot CH_2\cdot CO_2C_2H_5$, is of far greater importance than the free acid, owing to the very varied syntheses in which it finds application. This ester is obtained in the form of its crystalline sodium derivative by the action of sodium and alcohol (sodium ethoxide) on ethyl acetate (*see above*).

Ethyl acetoacetate (freed from sodium by means of acetic acid) is a liquid having a pleasant, fruity odour, and dissolves readily in alcohol or ether and slightly in water, in which it gives a red coloration with ferric chloride. It has a neutral reaction and a specific gravity of 1·030; it boils at 181° and is found in diabetic urine. When boiled with dilute alkali or dilute sulphuric acid, it undergoes *ketonic decomposition*, forming CO_2, acetone and alcohol:

$$CH_3\cdot CO\cdot CH_2\cdot CO_2C_2H_5 + H_2O = CO_2 + C_2H_5\cdot OH + CH_3\cdot CO\cdot CH_3.$$

With concentrated alcoholic potassium hydroxide, it undergoes *acid decomposition*, producing 2 mols. of acetic acid:

$$CH_3\cdot CO\cdot CH_2\cdot CO_2C_2H_5 + 2H_2O = C_2H_5\cdot OH + 2CH_3\cdot CO_2H.$$

Its great reactivity is due to the readiness with which one of the hydrogen atoms is replaceable by metals (Ba, Al, Zn, Ag, Cu, &c., in ammoniacal solution), especially by sodium. *Ethyl sodioacetoacetate*, $CH_3\cdot CO\cdot CHNa\cdot CO_2C_2H_5$, is a white solid soluble in water, while ethyl acetoacetate is soluble in alkali, from which it is reprecipitated by acids. The sodium is readily replaced by different alkyl groups by the action of the corresponding alkyl iodides (*see* the analogous syntheses with Ethyl Malonate, p. 309). Since the compounds thus obtained can be subjected to either acid or ketonic decomposition, it will readily be seen how very varied acids and ketones can be obtained by means of ethyl acetoacetate. For instance, the action of normal octyl iodide on ethyl sodioacetoacetate yields *methyl nonyl ketone*, a constituent of oil of rue:

$$CH\cdot{}_3CO\cdot CHNa\cdot CO_2C_2H_5 + I\cdot CH_2\cdot [CH_2]_6\cdot CH_3 =$$

$$NaI + CH_3\cdot CO\cdot CH{<}{\begin{matrix}[CH_2]_7\cdot CH_3\\ CO_2C_2H_5\end{matrix}}.$$

this compound, by ketonic decomposition, giving *methyl nonyl ketone*, which must hence have the normal structure $CH_3 \cdot CO \cdot CH_2 \cdot [CH_2]_7 \cdot CH_3$.

Further, by eliminating the sodium from ethyl sodioacetoacetate by means of iodine, the two residues combine, forming *ethyl diacetylsuccinate*:

$$2CH_3 \cdot CO \cdot CHNa \cdot CO_2C_2H_5 + I_2 = 2NaI + \begin{array}{l} CH_3 \cdot CO \cdot CH \cdot CO_2C_2H_5 \\ \quad\quad\quad\quad\; | \\ CH_3 \cdot CO \cdot CH \cdot CO_2C_2H_5 \end{array}$$

and this ester, on ketonic decomposition (boiling with 20 per cent. potassium carbonate solution), reacts with $2H_2O$ and gives $2CO_2$, $2C_2H_5 \cdot OH$ and *acetonyl-acetone*, $\overset{4}{C}H_3 \cdot \overset{3}{C}O \cdot \overset{2}{C}H_2 \cdot \overset{1}{C}H_2 \cdot CO \cdot CH_3$, which has a normal carbon-atom chain and is a 1 : 4 diketone.

Ethyl acetoacetate also combines with formaldehyde (in presence of diethylamine), with acetone and with ammonia; with aniline it gives diphenylcarbamide. With one or two mols. of sulphuryl chloride it gives *ethyl chloracetoacetate* (b.pt. 194°, sp. gr. 1·19 at 14°) or *ethyl dichloracetoacetate*, $CH_3 \cdot CO \cdot CCl_2 \cdot CO_2C_2H_5$, which boils at 206° and has the sp. gr. 1·293 at 16°.

LEVULINIC ACID, $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H$, is obtained synthetically by the acid decomposition of the product of reaction of ethyl acetoacetate and ethyl chloracetate. It can be prepared by boiling hexoses, cane-sugar, cellulose, gum, starch, &c., with concentrated hydrochloric acid.

It melts at 33° and boils at 239° with slight decomposition, or at 144° under 12 mm. pressure.

It is sometimes used in the printing of textiles.

KETO-ALCOHOLS

ACETONEALCOHOL or **ACETYLCARBINOL** (Propanolone), $CH_3 \cdot CO \cdot CH_2 \cdot OH$, is formed by heating either grape-sugar with fused potassium hydroxide or a mono-halogenated acetone with barium carbonate. It is a liquid which boils almost unchanged at 147° and reduces Fehling's solution even in the cold.

DIHYDROXYACETONE, $OH \cdot CH_2 \cdot CO \cdot CH_2 \cdot OH$, is formed together with glyceraldehyde by oxidising glycerol with nitric acid. It has a sweet taste and may indeed be regarded as a triose sugar. It crystallises in colourless plates and reduces Fehling's solution in the cold.

BUTAN-2-OL-3-ONE (Dimethylacetol), $CH_3 \cdot CO \cdot CH(OH) \cdot CH_3$, also reduces Fehling's solution and is obtained by reducing diacetyl. It is a liquid soluble in water and boils at 142°.

The higher homologue, *acetoisopropyl alcohol*, $CH_3 \cdot CO \cdot CH_2 \cdot CH(OH) \cdot CH_3$, b.-pt. 177°, is also known and is formed by the condensation (by means of alkali) of aldehyde with acetone. Removal of water from this compound yields **Ethylideneacetone**, $CH_3 \cdot CO \cdot CH : CH \cdot CH_3$, boiling at 122°.

DIKETONES

All diketones give mono- and di-oximes, and mono- and di-hydrazones, the latter (as with the aldehydes) bearing the name of osazones and being usually yellow. They often exhibit tautomerism and give rise to various cyclic condensation products.

DIACETYL or **α-DIKETOBUTANE** (Butandione), $CH_3 \cdot CO \cdot CO \cdot CH_3$, is prepared by the general method for diketones, namely, by treating methyl ethyl ketone, $CH_3 \cdot CO \cdot C_2H_5$, with amyl nitrite and a little HCl, the CH_2 group being transformed into $-C : NOH$, giving an *isonitrosoketone*, thus:

$$CH_3 \cdot CO \cdot CH_2 \cdot CH_3 + NO_2 \cdot C_5H_{11} \longrightarrow \begin{array}{l} CH_3 \cdot CO \cdot C \cdot CH_3 \\ \quad\quad\quad\quad\;\; \| \\ \quad\quad\quad\quad\; N \cdot OH \end{array};$$

when boiled with dilute sulphuric acid, this compound loses the hydroxyiminic group (as hydroxylamine), the diketone remaining.

It is a yellow liquid which has a penetrating odour, dissolves in water and boils at 88°, giving yellowish green vapour (sp. gr. 0·973 at 20°). With hydrogen peroxide, diacetyl is converted quantitatively into 2 mols. of acetic acid :

$$CH_3\cdot CO\cdot CO\cdot CH_3 + H_2O_2 = 2CH_3\cdot CO_2H.$$

ACETYLACETONE, $CH_3\cdot CO\cdot CH_2\cdot CO\cdot CH_3$. The best general method for preparing 1 : 3-diketones consists in treating an ester with sodium ethoxide :

$$R\cdot CO_2C_2H_5 + C_2H_5\cdot ONa = R\cdot C\begin{cases} ONa \\ OC_2H_5 \\ OC_2H_5 \end{cases};$$

this compound, when treated with a ketone, $R'\cdot CO\cdot CH_3$, loses 2 mols of alcohol and yields $R\cdot C\begin{cases} ONa \\ CH\cdot COR' \end{cases}$, from which the sodium is expelled by a dilute acid. This enolic form, $-C\begin{cases} OH \\ CH - \end{cases}$, readily passes into the ketonic form, $- CO - CH_2 -$, thus giving the compound $R\cdot CO\cdot CH_2\cdot CO\cdot R'$.

Another general method for obtaining 1 : 3-diketones consists in treating the sodium derivatives of acetylene homologues with an acid chloride and then acting on the acetylenic product with sulphuric acid, so that it combines with water :

$$\underset{\text{Amylacetylene}}{CH_3\cdot [CH_2]_4\cdot C \vdots Na} + \underset{\text{Acetyl chloride}}{CH_3\cdot CO\cdot Cl} = NaCl + CH_3\cdot [CH_2]_4\cdot C \vdots C\cdot CO\cdot CH_3 ;$$

the latter + $H_2O \longrightarrow CH_3\cdot [CH_2]_4\cdot CO\cdot CH_2\cdot CO\cdot CH_3$.

As in ethyl acetoacetate and ethyl malonate, the two hydrogen atoms of the methylene group between the two carbonyl groups are here also replaceable by metals, giving volatile compounds which are soluble in chloroform, benzene, &c., and differ from true salts, their solutions exhibiting very slight electrical conductivity.

Acetylacetone has a pleasant odour and boils at 137°. When boiled with water it yields acetone and acetic acid.

ACETONYLACETONE (γ-Diketohexane or Hexa-2 : 5-dione), $CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3$, is obtained by ketonic decomposition of the product of interaction of ethyl acetoacetate and ethyl chloracetate (*see also* Levulinic Acid) ; it boils at 194° and has an agreeable smell.

KETO-ALDEHYDES AND HYDROXYMETHYLENEKETONES

PYRUVIC ALDEHYDE (Methylglyoxal or Propanolone), $CH_3\cdot CO\cdot CHO$, is a volatile oil obtained by decomposing its oxime (isonitrosoacetone) with dilute acid (*see* Diacetyl).

ACETOACETALDEHYDE, $CH_3\cdot CO\cdot CH_2\cdot CHO$, was formerly thought to have been obtained in the free state, but more exact study has now shown the compound in question to be the unsaturated isomeride, HYDROXYMETHYLENEACETONE, $CH_3\cdot CO\cdot CH : CH\cdot OH$, which has an acid character and is obtained by the interaction of acetone and ethyl formate in presence of sodium ethoxide (*see* Ethyl Acetoacetate). It boils at 100° and readily condenses into 1 : 3 : 5-triacetylbenzene, $C_6H_3(CO\cdot CH_3)_3$.

F. POLYVALENT DIBASIC HYDROXY-ACIDS AND THEIR DERIVATIVES

TARTRONIC ACID (Hydroxymalonic or Propanoldioic Acid), $CO_2H\cdot CH(OH)\cdot CO_2H$, is formed by the spontaneous decomposition of nitrotartaric acid and is obtained synthetically by oxidising glycerol with potassium permanganate, by eliminating bromine from bromomalonic acid by the action of moist silver oxide, or by reducing Mesoxalic Acid, $CO(CO_2H)_2$. It crystallises with $\frac{1}{2}H_2O$ and melts at 184°, losing CO_2 and forming polyglycollides. It is soluble in water, alcohol, or ether.

MALIC ACID (Hydroxysuccinic or Butanoldioic Acid), $CO_2H \cdot CH(OH) \cdot CH_2 \cdot CO_2H$, occurs in abundance in unripe fruits (apples, grapes, quinces, and sorb-apples, from which it is extracted). Its crystals melt at 100° and it dissolves in water or alcohol and, to a slight extent, in ether. When subjected to dry distillation, it gives fumaric acid and maleic anhydride. Synthetically it is obtained from maleic or fumaric acid or asparagine, and also by the action of moist silver oxide on bromosuccinic acid, and by the reduction of tartaric acid by means of hydriodic acid.

As it contains an asymmetric carbon atom, malic acid forms three optically different stereoisomerides, all of which are known. Natural malic acid is lævo-rotatory, that derived from *d*-tartaric acid dextro-rotatory, and that obtained by other syntheses inactive but resolvable into active components by fractional crystallisation of the cinchonine salt.

It gives an acid calcium salt readily soluble, and a normal salt slightly soluble in water. The presence of the alcoholic group is proved by the formation of acetylmalic acid (*see* p. 189).

For the amido-derivatives, asparagine, &c., *see later*.

Of the *higher homologues of malic acid*, the following are known: Four isomeric acids, $C_3H_5(OH)(CO_2H)_2$ (*α*- and *β-hydroxyglutaric acids*, *itamalic* and *citramalic acids*); diaterebinic acid, $C_5H_9(OH)(CO_2H)_2$, which readily forms a lactone, and terebinic acid, $C_7H_{10}O_4$.

TARTARIC ACIDS, $CO_2H \cdot CH(OH) \cdot CH(OH) \cdot CO_2H$

These are dibasic and tetravalent, as they contain two secondary alcoholic groups. The presence of two asymmetric carbon atoms leads to the existence of four stereoisomerides, which have already been considered on p. 20: (1) ordinary or *d*-tartaric acid; (2) *l*-tartaric acid; (3) racemic or para- or di-tartaric acid; (4) i- or meso- or anti-tartaric acid.

They are obtained synthetically from dibromosuccinic acid, $CO_2H \cdot CHBr \cdot CHBr \cdot CO_2H$, and moist silver oxide, from glyoxal cyanohydrin, from glyoxylic acid by reduction, from mannitol by oxidation with nitric, acid and from fumaric or maleic acid by oxidation.

(1) ***d*-TARTARIC ACID.** This is the ordinary tartaric acid, which occurs abundantly as such, and as monopotassium tartrate (tartar) in many fruits —especially in the grape, and hence in wine, from which it is extracted in a manner to be described.

Dextro-rotatory tartaric acid forms hemimorphic, monoclinic prisms with a decided and pleasant acid taste. It is readily soluble in water or alcohol and almost insoluble in ether. One hundred parts of water dissolve 114 parts of the acid at 0°, 125·7 at 10°, 139·4 at 20°, 156·2 at 30°, 176 at 40°, 195 at 50°, 217·5 at 60°, 243·6 at 70°, 273·3 at 80°, 306·5 at 90°, and 343·3 at 100°. The acid melts at 170°, giving rise to various anhydrides and to pyruvic and pyrotartaric acids; ultimately it carbonises with an odour of burnt bread or, if the temperature is raised considerably, of burnt sugar.

Energetic oxidising agents convert it into tartronic acid or dihydroxytartaric acid and finally into formic acid, carbon dioxide, &c. In the hot, it reduces ammoniacal silver solutions (*see* p. 346 for a sensitive reaction for tartaric acid). Certain bacteria transform it into succinic acid. When burned, tartaric acid and tartrates emit an odour of burnt bread, thus differing from citric acid and citrates, which give a pungent odour.

Owing to the presence of alcoholic groups, tartaric acid, like glycerol, hinders the precipitation by alkali of many metallic oxides, *e.g.* of cupric oxide in Fehling's solution (containing caustic soda, copper sulphate, and sodium potassium tartrate; *see* Sugar Analysis), the intensely blue, soluble

compound, $\begin{array}{l} CO_2Na\cdot CH\cdot O \\ \quad\quad\;\; | \\ CO_2K\;\cdot\; CH\cdot O \end{array}\!\!\!\!>\!Cu$, being formed; this compound is not precipitable by alkalis, since the copper no longer functions as cation, but is contained in the anion, $\begin{array}{l} -O\cdot CO\cdot CH\cdot O \\ \quad\quad\quad\quad\;\; | \\ -O\cdot CO\cdot CH\cdot O \end{array}\!\!\!\!>\!Cu$, which migrates to the positive pole or anode when the salt is electrolysed.

Tartaric acid is used in dyeing, in the wine industry, in the preparation of aerated beverages (lemonade), in medicine, &c.

The following salts of tartaric acid may be mentioned, acid potassium tartrate being considered more in detail later.

ACID POTASSIUM TARTRATE (Cream of Tartar), $CO_2H\ CH(OH)\cdot CH(OH)\cdot CO_2K$, is slightly soluble in water or in dilute alcohol, and has a pleasant acid taste. For its commercial preparation, *see* Tartar Industry.

NORMAL POTASSIUM TARTRATE, $C_4H_4O_6K_2 + \frac{1}{2}H_2O$, is readily soluble in water and separates from highly concentrated solutions in monoclinic prisms.

SODIUM POTASSIUM TARTRATE (Rochelle Salt), $C_4H_4O_6NaK + 4H_2O$, is prepared by saturating cream of tartar solution with sodium carbonate. Copper and iron, present as impurities, are removed by means of hydrogen sulphide, the solution being then heated with good animal charcoal, filtered, concentrated and allowed to crystallise; the Rochelle salt separates in thick columns readily soluble in water and slightly so in alcohol. It is used to reduce silver salts in the silvering of mirrors and also for medicinal purposes and to prepare Fehling's solution. It costs about £7 per quintal.

CALCIUM TARTRATE, $C_4H_4O_6Ca + 4H_2O$, is insoluble in water but soluble in cold sodium hydroxide solution, from which it separates on heating as a jelly, which redissolves on cooling. It dissolves in acetic acid, thus differing from calcium oxalate.

TARTAR EMETIC (or Potassium Antimonyl Tartrate), $C_4H_4O_6(SbO)K + \frac{1}{2}H_2O$, is prepared by precipitating $SbOCl$ from a solution of $SbCl_3$ by means of water, boiling the precipitate with soda solution and dissolving the Sb_2O_3 thus formed in a solution of 4 or 5 times its weight of potassium hydrogen tartrate in 50 parts of water. After filtration and concentration the solution deposits, on cooling, efflorescent, trimetric pyramids, which are soluble in water (1 : 13 at 20°, 1 : 6 at 50°) but insoluble in alcohol. It is poisonous and is used in medicine as an emetic and in dyeing cotton as a mordant for basic dyes (price about £9 10*s.* per quintal). Germany imported 2019 quintals in 1908 and 3914 in 1909, the respective exports being 10,303 and 10,899 quintals in the two years.

(2) ***l*-TARTARIC ACID** differs from the *d*-acid only in the opposite sign of its rotation and in the opposed hemihedry of its crystals. Mixing of the concentrated aqueous solutions of the two acids results in development of heat and the formation of inactive tartaric acid.

(3) **RACEMIC ACID** (Paratartaric Acid), $(C_4H_6O_6)_2 + 2H_2O$, represents a mixture of dextro- and lævo-tartaric acids in equal proportions, and is hence optically inactive (*see* p. 20). When heated alone or, better, in presence of concentrated caustic soda solution, either the *d*-acid or the meso-acid (*see below*) is transformed into racemic acid. The latter is obtained from the mother-liquors of ordinary *d*-tartaric acid. The molecular weight, determined cryoscopically or from the vapour densities of the esters, corresponds with the simple molecule, $C_4H_6O_6$. It forms triclinic crystals which effloresce in the air, and is less soluble than the active acids. From *sodium ammonium racemate* crystals $(C_4H_4O_6)_2Na_2(NH_4)_2 + 2H_2O$, Pasteur separated those showing dextro- from those showing lævo-hemihedry, thus resolving racemic acid into its optically active constituents. Only in the crystalline state is the molecule of racemic acid regarded as double that of tartaric acid, whilst in dilute aqueous solution it is assumed to be decomposed completely into the two optical antipodes.

(4) **MESOTARTARIC ACID**, $C_4H_6O_6 + H_2O$, is optically inactive and is not merely a mixture of the active compounds. It is obtained by prolonged boiling of *d*-tartaric acid with excess of caustic soda. Its potassium salt is more soluble in water than those of the other tartaric acids.

THE TARTAR INDUSTRY

MANUFACTURE OF POTASSIUM BITARTRATE (Cream of Tartar or Potassium Hydrogen Tartrate). Although the crude prime material of this industry is very abundant in *Italy* in wine residues, it is only within the last few years that the working has been placed on a rational basis, the tartar being refined and tartaric acid prepared. Although these prime materials are subject to an export duty (1*s*. 9*d*. per quintal), the exportation from Italy amounted to about 178,000 quintals, worth £480,000, in 1905, and 178,500 quintals, worth £416,000, in 1910. The treatment of these products requires, besides special technical ability, also considerable quantities of fuel, and to this is partly due the difficulties of the Italian manufacturers.

Cream of tartar occurs abundantly in the green extremities of vine-shoots and in the grape, and part of it remains in the pressed *vinasse*. The vinasse of southern grapes contains as much as 4 per cent. of cream of tartar, and that of other grapes from 2 to 2·5 per cent. Vinasse that has not been in contact with the fermenting must, and that of second wines have practically no commercial value.[1]

Another portion of the cream of tartar which remains dissolved in the must gradually separates (*lees*) as fermentation proceeds—cream of tartar being less soluble in alcoholic liquids (wine)—and finally part of it is deposited as a crystalline crust on the walls of the casks during the winter, the solubility being less in the cold. One litre of water dissolves 3·2 grms. of tartar at 0°, 4 grms. at 10°, 5·7 grms. at 20°, 9 grms. at 30°, 13 grms. at 40°, 18 grms. at 50°, 24 grms. at 60°, 32 grms. at 70°, 45 grms. at 80°, 57 grms. at 90°, 69 grms. at 100°, 82 grms. at 110°, and 94 grms. at 120°. In an alcoholic liquid (with 10 per cent. of alcohol) the solubility is reduced almost to one-half; the solubility is also slightly diminished by the tartaric acid and increased by the mineral acids of the wine.

These crude products are of different colours according as they are obtained from white wines (white tartar) or red wines (red tartar), and according to the degree of purity.

Fresh *wine lees* (forming about 5 per cent. of the wine) are slimy, of a dirty red colour, and contain yeasts, colouring-matters, cream of tartar (10 to 25 per cent.), and calcium tartrate (6 to 20 per cent.). Italian wine lees are the richest in potassium bitartrate and the poorest in calcium tartrate. When removed from the vats, the lees are placed to drain in strong bags suspended by cords, the bags being afterwards tied up and pressed slightly in a press. They are then removed from the bags and dried in the air, being turned from time to time. When pressed and almost dry, they contain more than double as much tartar as when in the fresh state (about 10 per cent. of moisture, 6 to 10 per cent. of lime, 3 to 5 per cent. of sand, 25 to 40 per cent. of tartaric acid). In some large wineries the lees are passed directly to the filter-presses, cakes which are readily dried being thus obtained.

The crude tartar contains 45 to 70 per cent. of potassium bitartrate and calcium tartrate, and, if washed and crystallised once from hot water, this content may increase to 75 to 87 per cent.,[2] the product being then placed on the market under the name of *crystals*.

[1] One quintal of grapes yields 30 to 35 kilos of vinasse and 65 to 70 of must, so that the annual Italian production of 40,000,000 quintals would correspond with 20 to 25 million quintals of vinasse, containing, on the average more than 3 per cent. of tartar. The tartar is estimated by the method of Carles: a kilo of the vinasse is chopped and mixed, and 100 grms. weighed and boiled for 10 minutes with 700 c c of water in a litre flask, the liquid being subsequently made up to the mark with distilled water. Five hundred cubic centimetres of the filtered solution are concentrated to about 100 c.c., 70 c c. of saturated calcium acetate solution being then added to the boiling liquid; after mixing, the liquid is allowed to cool for 12 hours, the precipitated calcium tartrate being then collected on a tared filter, washed with water, dried at 60°, and weighed. Multiplication of the result by 2 and deduction of 5 per cent. (to allow for the volume occupied by the vinasse in the litre flask) gives the calcium tartrate per 100 grms of vinasse; further multiplication by 0·723 gives the corresponding amount of potassium hydrogen tartrate. Ciapetti has rendered this method more exact by transforming the calcium tartrate (by potassium bioxalate in the hot) into potassium hydrogen tartrate, filtering and washing the residue, concentrating the filtrate and adding alcohol to precipitate the potassium bitartrate; the latter is washed, redissolved in hot water and titrated with decinormal caustic soda solution (*see below*, Analysis of Tartar)

[2] **Analysis of Tartar.** Tartar being a rather expensive substance (£6 to £8 per quintal), it is frequently adulterated with sand, gypsum, &c. It is always bought and sold on its strength, the potassium bitartrate or the total tartaric acid (thus including both the calcium tartrate and the free tartaric acid) being determined.

A homogeneous sample is finely ground and sieved, the residue being again ground.

A test which is not very exact but is rapid and largely used is the *direct titration test* The coarse *impurities*, sand, clay, sulphur, woody matter, yeasts, &c., are estimated by boiling a known weight of the crude tartrate with water acidified with HCl, and collecting, washing, drying, and weighing the residue on a tared filter; the residue is sometimes ashed.

The calcium carbonate is determined by treating with an acid in the calcimeter and measuring the carbon dioxide evolved, and the total lime, including that of the tartrate, by calcining a given weight of the tartar,

As a rule 60 to 70 per cent. of the total tartar is extracted from the vinasse after the alcohol has been distilled off with steam in the manner indicated on p. 143. The forms of apparatus there shown give almost saturated, boiling solutions of tartar (the remaining vinasse being centrifuged or pressed to remove all the tartaric liquors), which are allowed to cool in shallow, wooden vessels. In these vessels are hung, after some time, strings studded with tartar crystals, on which less impure crystals gradually form. The deposit forming on the walls of the vessels is of a less degree of purity, and that on the bottom contains many coloured impurities. In 5 to 6 days the crystallisation is complete, more rapid and complete separation being attained in very cold places or by the use of artificial cooling. The mother-liquors decanted from the tartar may be utilised again for extraction of vinasse, but when they become too rich in impurities or mucilaginous substances, they are either used as fertilisers, since they contain potassium salts, or, better, are treated (Carles, 1910) at boiling temperature with 60 grms. of potassium ferrocyanide per hectolitre, the iron, alumina, copper, &c., present being thus removed; the clarified liquid is treated with lime to separate calcium tartrate, the potassium salts being recoverable from the filtered solution by the Alberti process (*see later*).[1] The dregs deposited during the extrac-

dissolving out the potassium carbonate, treating the residual calcium carbonate with excess of standard nitrous acid solution, and measuring the excess of the acid by titration with soda solution. The *total lime* is, however, best estimated by dissolving 2 grms in HCl, neutralising with ammonia, precipitating with ammonium oxalate, and heating on a water-bath, the precipitate being subsequently collected on a filter, ignited in a platinum crucible and weighed as CaO.

The *titration test* of the quantity of acid potassium tartrate is carried out by dissolving a weighed amount (2 to 3 grms) of the tartar in water and titrating the boiling solution with N/4-sodium hydroxide solution, using very sensitive litmus paper as indicator; 1 c c. of N/4-caustic soda solution corresponds with 0 047 grm of potassium bitartrate. Multiplication of the amount of bitartrate by 0 798 yields the corresponding amount of tartaric acid

For international trade, the potassium bitartrate is nowadays estimated by the *filtration process*, which largely excludes errors due to the presence of tannin substances and other impurities which also react with litmus:

2 35 grms of the substance (crude tartar, sludge or lees) are heated to boiling for 5 minutes with 400 c c. of water in a 500 c c flask; water is again added and the whole cooled, made up to 500 c c, mixed and filtered through a folded filter Of the filtrate 250 c c are heated to boiling and titrated with N/4-potassium hydroxide solution (standardised with pure bitartrate), sensitive litmus paper being used as indicator.

For more exact determinations, *Kammer's recrystallisation method* is employed:

4 7025 grms. of substance (molecular weight of tartar divided by 40) are heated to boiling with 30 to 40 c c of water in a 100 c c flask, the solution being then neutralised with N/4-caustic soda, of which 1 to 2 c c in excess are added. The volume is made up to 100 c c., and of the filtered solution, 20 c c. are rendered decidedly acid with acetic acid and treated with 100 c c. of a mixture of alcohol and ether, which separates the potassium bitartrate completely in crystals These are collected on a filter, washed with alcohol and ether, redissolved in boiling water, and titrated with N/20-soda solution.

Determination of the total tartaric acid This gives the total content of potassium bitartarate, calcium tartrate, and free tartaric acid. The Goldenberg-Geromont hydrochloric acid process, which was formulated as follows at the Congress of Applied Chemistry at Turin in 1902, is generally used:

Six grammes of the substance are treated for 8 to 10 minutes in a small beaker with 9 c.c (for products poor in tartar) or 18 c.c (for richer products) of cold HCl (sp gr. 1 10), the whole being then washed into a 100 c c flask, made up to volume, mixed, and passed through a dry pleated filter. Fifty cubic centimetres of the filtrate are *boiled* for 10 to 15 minutes in a tall 250 to 300 c c. beaker with 5 (or 10) c c of concentrated potassium carbonate solution (66 grms in 100 c c of water), the liquid being then washed into a 100 c.c flask, cooled, made up to volume, and filtered through a pleated filter Fifty cubic centimetres of this filtrate are taken to dryness in a half-litre dish, redissolved in 5 c c of boiling water, and vigorously stirred with 4 to 5 c c of glacial acetic acid; when the liquid is cold, 100 to 110 c c of 96 per cent. alcohol are mixed in, and the potassium bitartrate allowed to deposit. This is filtered under pressure, the dish, rod, and filter being repeatedly washed with alcohol. The filter and the bitartrate are then washed into the same dish with boiling water, with which the volume is made up to about 300 c c. The liquid is then boiled and titrated with N/4-alkali, the end-point being determined with sensitive litmus paper.

To eliminate the error due to the volume occupied by the impurities in the original flask, 0 7 per cent is deducted from the total content in the case of low-grade tartars (containing less than 20 per cent. of bitartrate) and 0 7 − ($n \times 0{\cdot}02$) in the case of those containing 20 to 50 per cent, n being the excess percentage over 20; beyond 50 per cent. the correction becomes almost zero.

[1] In many places the vinasse is placed in vats fitted with false bottoms, steam being passed in below while a spray of mother-liquor (*red liquors*) falls from above; as many hectolitres of these liquors are employed as there are quintals of vinasse. In this manner, the first solution of the tartar is obtained almost boiling and almost saturated, it is purified by percolating slowly through the vinasse (the steam expels the air and condenses). A second extraction gives a less completely saturated solution, which is utilised for further extractions Finally, the vinasse is not pressed but is washed with water and a little hydrochloric acid to extract the calcium tartrate, exhaustion being then obtained by means of cold water (*Tarulli's method*). The mother-liquors from the crystallisation, when they become too impure or, in some cases, even after the first crystallisation, are treated with milk of lime to precipitate all the dissolved tartar, while the liquors from the second and third extractions are used for fresh quantities of vinasse.

To obtain purer solutions from the vinasse, to avoid losses occasioned by the presence of lime in the water, and to extract calcium tartrate at the same time, Ciapetti exhausts the vinasse with dilute solutions of sulphurous and hydrosulphurous acid—which do not dissolve the colouring-matters or the pectic or albuminoid substances—and allows refined, white cream of tartar (!) to crystallise out; the mother-liquors are utilised further. This method was tried in various works, but did not give the results expected of it. Extraction on the Ciapetti system may also be carried out in the series of stills used for the distillation of the vinasse (*see later*, Tartaric Acid, Gladysz Process).

The fresh vinasse or the deposits, if not to be worked up at once, may be kept for some months if tartaric

tion of the cream of tartar from the vinasse contain, in the dry state, 30 to 60 per cent. of potassium bitartrate and 10 to 20 per cent. of calcium tartate.

The *refining* of crude tartar from vinasse, lees, &c., is very difficult with the poorer products, and in practice rich and poor materials are often mixed so as to give a content of 60 to 65 per cent. when a highly refined tartar is not required.

The crude tartar or other mixture should first be ground and then sieved to remove pieces of wood and other impurities. In order to destroy certain impurities and protein substances and hence hasten the filtration of the subsequent aqueous solutions, the lees or low-quality tartar are heated in revolving iron cylinders until the temperature reaches 160° to 180°, the loss in weight being 8 to 12 per cent. It is then introduced into a perforated copper cylinder placed almost on the bottom of a large wooden vessel furnished with copper or aluminium steam coils. Care is taken not to use an excess of water, which would involve waste of fuel, and generally 6 to 8 parts of water are taken per 1 part of tartar. A hood is usually fitted over the vessel to carry off the steam from the boiling solution. In order to transform the calcium tartrate present into potassium bitartrate, 3 kilos of hydrochloric acid (20 Bé.), and 3 kilos of potassium sulphate (previously dissolved in 20 litres of water) are added to the water per kilo of lime (CaO) contained in the calcium tartrate (*see* method of determination given above). The liquid is stirred occasionally, boiled for an hour and allowed to settle for about a further hour, after which either the bitartrate solution is decanted by means of a tap a short distance from the bottom, or the whole mass is passed through a filter-press. The liquid is left to cool in a cold place in ordinary crystallising vessels, or, better, in copper or aluminium basins, a somewhat impure and reddish brown tartar crystallising out. Rather purer tartar may be obtained by collecting the crystals separating while the solution is cooling to 35° to 40°, small crystals being ensured by occasional stirring; the tepid mother-liquors are then decanted and crystallised in a cold place.

The brown mother-liquors are used repeatedly to dissolve fresh quantities of the crude tartar substances in the hot. The brown crystals are detached from the crystallising vessels by means of suitable spatulas and redissolved, in a wooden vessel similar to that previously used (with a perforated bottom for the crystals), in 10 to 12 times their weight of water, which is boiled by indirect steam supplied through copper or aluminium coils. Decoloration is effected by adding, after half an hour's boiling, about 1 per cent. of animal charcoal (well washed with hydrochloric acid and thoroughly rinsed; for very impure tartar from lees as much as 6 to 8 per cent. of animal charcoal is used.) After mixing and an hour's boiling, about 1 per cent. of kaolin free from chalk (washed with HCl) is well mixed in in the hot and the liquid either filter-pressed or left for 2 to 3 hours so that the kaolin may carry down all the suspended charcoal. In some cases the solutions are clarified by adding tannin and gelatine (50 grms. of the latter and 250 of tannin dissolved separately) after the kaolin and before filtration. The pale yellow, clear solution is decanted (the first and last portions, which are rather turbid, being kept separate) and crystallised in wooden crystallising vessels or in copper or aluminium basins; in three or four days the crystallisation is complete. The mother-liquors are used to dissolve fresh brown crystals, since they contain a little free tartaric acid which dissolves many of the impurities better than water does, and so results in the separation of purer crystals. After the removal of the mother-liquor, the crystals are washed repeatedly with very pure water (condensed), a trace of hydrochloric acid being added to the first washing water if the crystals show any superficial turbidity. They are finally dried on cloths in a desiccator at 60° with the help of a current of air.

In France and also in certain Italian factories, Carles has applied a method of extracting the tartar which consists in treating 100 parts of the crude, powdered tartar with 400 parts of water at 70°, containing sufficient sodium carbonate to transform all the potassium bitartrate into the highly soluble sodium potassium tartrate (1 : 1·2). This solution is decanted or filtered and treated with more than the amount of hydrochloric or sulphuric acid necessary to neutralise the soda added; this leads again to the formation of the slightly soluble potassium bitartrate, which crystallises out (96 per cent. purity) on cooling. Vinasse is also extracted more readily by this alkaline method.

fermentation—which would destroy part of the cream of tartar—is prevented, either by addition of 0·05 per cent. of sodium thiosulphate or by maintaining the vinasse strongly compressed, under chalk and sand, in wooden vats (tartaric fermentation is caused principally by *Bacillus saprogenes vini*). The yields of tartar and alcohol are determined on a small quantity (5 kilos) of the vinasse in a small Savalle distilling and macerating apparatus.

The recent process of Cantoni-Chautems and Degrange (1910) refines the tartar almost in the cold and effects a marked economy of chemical products. This method serves well also for poor products (20 per cent. lees), which are heated as described above and washed first with cold sodium carbonate solution in a series of vessels, next slightly with water, and finally, slowly and systematically with dilute hydrochloric acid.

In the first case, sufficient soda is added to convert the tartar almost completely into sodium potassium tartrate, which can be extracted with the minimum quantity of water. The treatment with hydrochloric acid dissolves the remainder of the tartar and also the calcium tartrate. The amount of the acid used is chosen so that, when the alkaline and acid solutions are united, it neutralises the soda first used. The hydrochloric acid solution is mixed previously with the amount of oxalic acid required to precipitate the whole of the lime present in the crude tartar as calcium tartrate, while sufficient potassium chloride is added to the alkali solution to transform all the tartaric acid, existing as calcium tartrate, into potassium bitartrate. Mixing of the two solutions in the cold results in the precipitation of almost all the cream of tartar in a white, highly pure state, and of the calcium oxalate. After filtering, the dark mother-liquors are kept for subsequent operations, while the solid residue is treated with the calculated (on the solubility of the tartar) quantity of water at 90°, a little oxalic acid being added to render the calcium oxalate less soluble. The mass is then filtered or centrifuged (if necessary, decolorised with a small amount of animal charcoal), the clear liquid, on cooling, depositing refined tartar of a purity of 99 to 99·5 per cent. The mother-liquor is used to initiate the solution of further quantities of crude tartar, &c. Oxalic acid may be recovered from the calcium oxalate.

A process which allows of the conversion of calcium tartrate into potassium bitartrate consists in boiling, say, 100 kilos of the calcium tartrate (85 per cent.) with 1500 litres of water and 53·5 kilos of potassium bisulphate (or a mixture of 35 kilos of the neutral sulphate and 24·6 kilos of sulphuric acid at 60° Bé.) for half an hour, decanting and filtering the liquid, from which pure potassium bitartrate (up to 98 per cent.) crystallises on cooling.

This process is a modification of that of Martignier (Fr. Pat. Nov. 23, 1889), who transforms calcium tartrate into normal potassium tartrate by decomposition with normal potassium sulphate; after filtration and concentration and addition of the calculated amount of sulphuric acid, the solution deposits potassium tartrate.

If the cream of tartar crystals are not pure but contain small proportions of calcium tartrate, they do not give perfectly clear solutions in water. When the pale mother-liquors from the final refining are somewhat impure, they are used in place of the brown liquor to dissolve the crude material, the highly impure brown liquors being used in the manufacture of tartaric acid or added in small amounts to the prime tartaric materials.

STATISTICS AND USES. The exports of crude tartar substances (vat deposits, wine lees, &c.) from Italy are as follow: in 1887, 150,000 quintals, worth £1,000,000; in 1896, 147,566, and in 1903, 164,000 quintals. The importation of crude tartar and lees amounted to 1424 quintals in 1887, 3975 quintals in 1896, 2356 quintals in 1902, and 3356 quintals in 1903.

The total Italian production of tartar, &c., in 1905 has been estimated at £1,600,000, but this is probably in excess of the truth, since the *world's production* was valued at about £2,800,000. Crude tartar and lees pay an export duty from Italy of 1*s.* 9*d.* per quintal, no import duty being levied; refined tartar pays an import duty of 3*s.* 2*d.* Italy contains about 200 crude cream of tartar works, but only very few manufacturing refined tartar.

In 1905 Germany imported, for refining, 26,000 quintals of crude tartar, worth £129,600; 26,914 quintals in 1908, and 20,263 quintals in 1909, the exports being 12,250 and 11,535 quintals respectively. In 1890, more than 51,000 quintals were imported, and in 1896 about 57,000 quintals, the corresponding exportation being about 5000 quintals of the refined product. France produces annually 61,000 quintals of refined cream of tartar. The imports of tartaric acid into England were 1850 tons in 1909 and 2250 tons (£203,365) in 1910, when the exports were valued at £31,300; in 1911 the imports amounted to £200,300, and the exports to £38,240. The imports of cream of tartar were 3550 tons in 1909, 4100 tons (£307,000) in 1910, and £301,940 in 1911.

Crude cream of tartar is bought and sold at 11½*d.* to 14½*d.* per unit of strength, and the refined at 1*s.* 7*d.* or more.

Cream of tartar is largely used in dyeing, in the bichromate mordanting of fast

wool dyes, &c., and in the printing of textiles. Considerable quantities are used in the United States for preparing powder which is added to dough to render the bread light and elastic; this powder contains 69 per cent. of tartar and 31 per cent. of sodium bicarbonate.

MANUFACTURE OF TARTARIC ACID. This acid is prepared by decomposing its salts (cream of tartar, lees, calcium tartrate, &c.), the dark mother-liquors and the deposits and sludges of cream of tartar factories being most commonly employed.

Attempts were at one time made to liberate the acid from its soluble salts by treating these, in hot solutions, with hydrofluosilicic acid, which separates as insoluble potassium fluosilicate, the solution of tartaric acid remaining being filtered, concentrated and crystallised. The potassium fluosilicate is treated with calcium carbonate to convert it into insoluble calcium fluosilicate, which yields hydrofluosilicic acid under the action of an energetic acid. Tartaric acid has also been prepared by treating solutions of its salts with barium carbonate and then with barium chloride, the latter precipitating the neutral potassium tartrate partly formed by the former reagent.

At the present time, however, the method most commonly used consists in treating boiling cream of tartar solutions with milk of lime or powdered calcium carbonate. In this way half of the tartar is converted into insoluble calcium tartrate and the other half into the soluble normal potassium tartrate, the latter being then separated as the insoluble calcium salt by addition of calcium sulphate or chloride:

$$2C_4H_5O_6K + CaCO_3 = H_2O + CO_2 + C_4H_4O_6Ca + C_4H_4O_6K_2;$$
$$C_4H_4O_6K_2 + CaSO_4 = K_2SO_4 + C_4H_4O_6Ca.$$

The acid is liberated from calcium tartrate by means of sulphuric acid:

$$C_4H_4O_6Ca + H_2SO_4 = CaSO_4 + C_4H_6O_6.$$

According to the nature of the materials employed, various procedures are adopted.

Crude tartar is freed from coarser impurities by passing through a wide-meshed sieve, heated if necessary (*see above*), ground to a fine granular condition and placed in a wooden vessel, where it is treated with 8 to 10 times its weight of boiling water. The mass is well mixed with a stirrer and heated to boiling by a steam jet, most of the tartar then dissolving. A paste of calcium hydroxide (sieved) is then added until a small portion of the liquid gives only slight effervescence with calcium carbonate (as a rule, 160 grms. of quick-lime, made into a 10 per cent. paste, are required for each kilo of potassium tartrate), the mixture being then boiled for 15 minutes.

In this way calcium tartrate is precipitated, while normal potassium tartrate remains in solution. The latter is then precipitated as calcium salt by boiling with a slight excess of gypsum or of calcium chloride solution (300 grms. of the chloride per kilo of tartrate used) for about two hours; a little precipitated calcium carbonate is finally added to precipitate the neutral tartrate as completely as possible. In some cases, however, the liquid is left slightly acid to prevent separation of iron and aluminium salts. It is, indeed, necessary to ensure the absence from the various reagents (lime, chalk, gypsum, &c.) of iron, aluminium, and especially magnesium, the latter forming magnesium tartrate, which is ultimately found as magnesium sulphate in the tartaric acid after the calcium tartrate has been treated with sulphuric acid. The boiling liquid is kept mixed and is afterwards either allowed to cool to 40° and decanted or passed immediately to the filter-press; after repeated washings with hot and cold water, the crude, dry tartrate is placed on the market and the filtrate either rejected or evaporated to obtain the potassium chloride present. But where the calcium tartrate is converted into tartaric acid, it is not necessary to filter and dry it, the tartrate, after the first decantation, being mixed with various separate amounts of water, which are drawn off when the precipitate settles. The calcium tartrate remaining can then be treated in the same vessel with sulphuric acid as described above.

The procedure is rather more complicated in the case of *wine lees* (sediments, sludge, &c.), as the tartrate cannot be extracted merely by treatment with water and filtration, owing to the presence of considerable amounts of mucilaginous protein substances (ferments), which impede filtration. The moist lees (drained in bags and pressed) contain as much as 8 per cent. of cream of tartar, or, if dried in the sun, still more.

These lees are nowadays worked by the Dietrich and Schnitzer process (1865): they are first powdered and mixed by means of stirrers and then heated for 5 to 6 hours in iron

autoclaves (4 metres high and 1·4 wide for 15 quintals of lees) at 4 to 5 atmos. pressure, direct steam being admitted by copper coils and the air first allowed to escape. The albuminoids are thus coagulated together with large quantities of colouring-matters, and the mass can then be easily filtered, but before this, it is discharged into a lead-lined wooden vessel (holding 10 to 12 cu. metres) containing 3 cu. metres of water and the amount of hydrochloric acid (20° to 22° Bé.) corresponding with the quantity of tartar previously determined (100 kilos of potassium bitartrate require 60 kilos of hydrochloric acid at 20° Bé., or 54·5 kilos at 22° Bé.). The mass is well mixed and passed through the filter-press, in which it is washed with water. The tartaric acid is then separated from the solution as calcium tartrate, as described above.

Lees may be treated economically and well by the process of Cantoni, Chautems, and Degrange described above.

To utilise the potash salts of the filtrate from the calcium tartrate, A. Alberti (U.S. Pat. 757,295, 1910) decomposes the organic substances in the hot with calcium chloride, filters and concentrates in a vacuum.

The second phase of the manufacture of tartaric acid consists in the decomposition of the calcium tartrate by means of sulphuric acid (*see above*) and in the subsequent crystallisation of the tartaric acid.

The calcium salt in the decantation or washing vessels, or as cakes from the filter-presses, is broken up and suspended in 5 to 6 times its weight of water in lead-lined wooden vessels furnished with stirrers covered with lead and with coils for indirect steam-heating. After the liquid paste has been well stirred, the sulphuric acid, previously diluted, is added in such amount that, after an hour's stirring at 60° to 70°, there is still a slight excess of sulphuric acid, detectable by the faint green coloration imparted to a solution of methyl violet. Too great an excess of sulphuric acid produces blackening of the tartaric acid solution during concentration, whilst deficiency of sulphuric acid results in the formation of turbid, impure tartaric acid crystals; but when a little free sulphuric acid is present, fine shining crystals are obtained. Usually 1 kilo of sulphuric acid at 66° Bé. is employed per 3 kilos of dry calcium tartrate. The solution is boiled for a couple of hours, left to cool, and the calcium sulphate which forms separated by means of a filter-press, washed with a little tepid water (this being added to the filtrate), and then with much cold water (this being used for treating subsequent quantities of calcium tartrate). The tartaric acid solutions were at one time concentrated in shallow, lead-lined, wooden vessels containing leaden steam-coils. But nowadays concentration is carried out in vacuum pans which are similar to those described later in dealing with the sugar industry and are of lead and of considerable thickness.

The liquid is evaporated until it becomes almost syrupy, and is then discharged into wooden vessels containing stirrers, which cool the concentrated solution rapidly and thus cause the tartaric acid to separate in small crystals. The cold mass is quickly separated from the mother-liquor in a centrifuge, the crystals being washed with a fine spray of cold water. The mother-liquors are then concentrated until they give crystals, this process being carried out three times; they are finally treated with milk of lime to separate the residual tartaric acid as calcium tartrate, which is filtered and worked up with the other calcium tartrate. The tartaric acid crystals are dissolved in one-half their weight of boiling water (if necessary, the solution is decolorised with animal charcoal and filtered) and the liquid left to crystallise, the crystals thus obtained being centrifuged and dried on sheets of lead in a current of air at 30°; the mother-liquors are used to dissolve fresh quantities of the small crystals.

The final *yield* is about 90 to 95 per cent. of the total tartaric acid in the prime materials when these are poor (*e.g.* lees with 20 to 25 per cent. of tartar) or 97 to 99 per cent. when richer prime materials (70 to 80 per cent. of tartar) are used.

A process still little used but worked successfully for many years in the Montredon factory near Marseilles is that of Gladysz (Ger. Pat. 37,352, October 15, 1885), which is based on the following observations: (1) When calcium tartrate is suspended in water and saturated with sulphur dioxide, soluble calcium bisulphite is formed and the tartaric acid liberated; (2) when this solution is heated to 66°, the sulphurous acid is expelled and all the tartaric acid precipitated as pure crystallised calcium tartrate; (3) if in (1) potassium bitartrate is used instead of calcium tartrate, potassium bisulphite and tartaric acid are formed, and on heating the liquid to 80°, sulphur dioxide is evolved and pure

potassium bitartrate separated in a crystalline state; (4) potassium tartrate, when treated with calcium bisulphite, gives potassium bisulphite and calcium bitartrate; the latter separates at 100°, when the potassium bisulphite gives, with lime, calcium bisulphite and caustic potash, which can also be utilised.

In practice Gladysz proposed to suspend the tartar in lumps in lead-lined wooden vessels, and into these—hermetically sealed and arranged in a series of five or six—to pass sulphur dioxide. The solutions (10° to 12° Bé.) thus obtained are sent to the concentration apparatus, which communicates with towers to condense the sulphur dioxide (*see* vol. i, p. 245). When the latter is completely evolved, the liquid is kept at 125° for a short time to separate crystalline calcium tartrate, which is collected by means of a centrifuge, while the solution is concentrated further and allowed to cool in shallow lead-lined wooden vessels to deposit the potassium tartrate. As a rule, however, the hot potassium tartrate solution is treated directly with calcium chloride and a little lime, so that it yields insoluble calcium tartrate, which is more easily separated. From this calcium tartrate, pure tartaric acid is then obtained in the ordinary way. Although theoretically no sulphur dioxide should be lost in this process, in practice about 15 per cent. is lost in winter and 20 per cent. in summer.

The Gladysz process, somewhat modified by Ciapetti, is used in Italy in the manufacture of tartar from vinasse, lees, &c. (*see* p. 338).

USES AND STATISTICS OF TARTARIC ACID. This acid is used in considerable quantities to replace the more expensive citric acid in the preparation of beverages, liquors, and aerated waters, and in wine-making. Large quantities are consumed in the mordanting of wool and silk, to reduce chromium salts, &c., in the printing of textiles, manufacture of dyes, photography, medicine, &c. Refined tartaric acid pays an import duty in Italy of 8*s*. per quintal and in the United States and Spain of 25 per cent. *ad valorem.*

Italy possesses four tartaric acid factories: at Carpi, Agnano (Pisa), Barletta, and Milan. The last two are the more important, and are able to produce together as much as 30,000 quintals per annum.

The *world's production* in 1905 was about 110,000 quintals, of which Italy produced 6700 quintals; England and the United States, each more than 25,000; Germany, about 15,000; France, about 8000 (13,000 in 1910); and Austria-Hungary about 10,000 quintals. Germany exported 17,000 quintals of the refined acid in 1908 and 19,000 in 1909, in which year the importation was 3240 quintals. In 1909, England imported 18,500 quintals and exported 3500. Italy imported 981 quintals, worth £10,200, in 1902; 1050 quintals in 1905; 1658 in 1907; 1574 quintals, worth £15,216, in 1909; 2976 quintals (one-third from Austria), worth £27,380, in 1910. Exports from Italy amounted to 17,000 quintals in 1907; 19,300 in 1908; 15,050, worth £141,480, in 1909, and 21,774 quintals, worth £195,966, in 1910. In 1907, four Russian factories, worked by a syndicate, produced 6000 quintals of tartaric acid and sold it at £20 per quintal. In 1911 the United States imported 12,500 tons (£575,400) of tartar.

In 1904, Argentine imported 950 quintals, and in 1909, 4650 quintals. But there is now a factory at Buenos Ayres which can produce 3500 quintals per annum.

Pure tartaric acid, which formerly cost £14 per quintal, is now sold at £10 to £10 8*s*.

ARTIFICIAL TARTARIC ACID. In 1889 a process was patented by Basset, and in 1891 a similar but improved one by Naquet for obtaining tartaric acid from starch (1 to 5 of water) by saccharifying with an equal weight of hot sulphuric acid (51° Bé.), then adding double this quantity of sulphuric acid and almost as much sodium nitrate and heating at 100°. When the reaction becomes very vigorous, the temperature is moderated and the heating continued at 80° to 90° for 2 to 3 days, the evaporated water being first replaced and the liquid concentrated to a syrup when evolution of gas ceases. In this manner all the saccharic acid is decomposed; the sulphuric and oxalic acids are then neutralised with calcium carbonate and the tartaric acid subsequently worked up in the usual manner by way of its calcium salt.

One hundred kilos of starch should give theoretically 140 of calcium tartrate corresponding with 56 kilos of tartaric acid, but in practice the yield of the acid does not exceed 55 to 60 per cent. of this theoretical amount.

TRIHYDROXYGLUTARIC ACID, $CO_2H \cdot [CH(OH)]_3 \cdot CO_2H$, should exist in four stereoisomeric forms, of which the dextro-, lævo- and racemic (m.pt. 127°) compounds

are known. They are obtained by the oxidation of xylose or arabinose, and, on reduction, give glutaric acid, their constitution being thus confirmed.

SACCHARIC ACID, $CO_2H\cdot[CH(OH)]_4\cdot CO_2H$, forms ten stereoisomerides, which are all known and are closely related to the sugars. Saccharic acid is formed as a rule in the oxidation of sucrose, glucose, mannitol, and starch (*e.g.* with nitric acid). It is deliquescent and soluble in water, and when heated or fused is converted into *saccharone,* which is a dextro-rotatory lactone melting at about 150°.

MUCIC ACID, $CO_2H\cdot[CH(OH)]_4\cdot CO_2H$, is the stereoisomeride of saccharic acid which is constantly inactive. It is obtained on oxidising lactose, dulcitol, gum, &c., and forms a white powder very slightly soluble in water.

KETONIC DIBASIC ACIDS

Ethers of these acids, like those of β-ketonic acids (ethyl acetoacetate, &c.; *see* p. 332), show both ketonic and acid decompositions, and also a new method in which carbon monoxide separates.

MESOXALIC ACID (Dihydroxymalonic Acid), $CO_2H\cdot CO\cdot CO_2H + H_2O$ or $CO_2H\cdot C(OH)_2\cdot CO_2H$, shows ketonic behaviour in agreement with the first formula, but the molecule of water cannot be separated from the deliquescent prisms even at 100°, and, further, derivatives (esters, &c.), are known which correspond better with the second formula, whilst the latter also explains well why mesoxalic acid, when heated with water, loses CO_2 and gives glyoxylic acid, $CO_2H\cdot CH(OH)_2$. The structure of the acid likewise follows from its formation by the action of barium hydroxide on ethyl dibromomalonate:

$$CBr_2(CO_2C_2H_5)_2 + Ba(OH)_2 = BaBr_2 + C(OH)_2(CO_2C_2H_5)_2.$$

Its ketonic constitution is confirmed also by the fact that it gives tartronic acid, $CO_2H\cdot CH(OH)\cdot CO_2H$, on reduction.

OXALACETIC ACID (Butanonedioic Acid), $CO_2H\cdot CH_2\cdot CO\cdot CO_2H$, is not known in the free state, but is formed as ether by condensation of ethyl oxalate and ethyl acetate in presence of sodium ethoxide (*see* Ethyl Acetoacetate). It also splits up in two ways according as it is treated with dilute sulphuric acid (giving pyruvic acid, CO_2, and alcohol) or with alkali (giving oxalic and acetic acids). Being a ketone, it forms an oxime.

The alcoholic solution is coloured dark red by ferric chloride and hence corresponds with the enolic form, $C_2H_5\cdot O\cdot CO\cdot CH:C(OH)\ CO_2C_2H_5$. This ester, like ethyl acetoacetate, is used in many syntheses, the hydrogen of the methylene group being replaceable by sodium, &c.

ACETONEDICARBOXYLIC ACID (Pentanonedioic Acid), $CO_2H\cdot CH_2\cdot CO\cdot CH_2\cdot CO_2H$, forms crystals which melt at 135°, losing $2CO_2$, and giving acetone. It is formed by the action of concentrated sulphuric acid, in the hot, on citric acid:

$$\begin{array}{l} CH_2\cdot CO_2H \\ | \\ C\!<\!\begin{smallmatrix} CO_2H \\ OH \end{smallmatrix} \\ | \\ CH_2\cdot CO_2H \\ \text{Citric acid} \end{array} = CO + H_2O + \begin{array}{l} CH_2\cdot CO_2H \\ | \\ CO \\ | \\ CH_2\cdot CO_2H \end{array}$$

The constitution of citric acid is shown by its formation from acetonedicarboxylic acid by the action of hydrogen cyanide and subsequent hydrolysis.

The hydrogens of the two methylene groups are replaceable by sodium, so that this acid can be used in syntheses similar to those effected by ethyl acetoacetate.

DIHYDROXYTARTARIC ACID, $CO_2H\cdot CO\cdot CO\cdot CO_2H + 2H_2O$, or, better, $CO_2H\cdot C(OH)_2\cdot C(OH)_2\cdot CO_2H$, melts and decomposes at 98° and forms a sodium salt, which is sparingly soluble and decomposes readily into CO_2, and sodium tartronate, $CO_2H\cdot CH(OH)\cdot CO_2Na$.

It is obtained by the action of nitrous acid on an ethereal solution of pyrocatechol, guaiacol, &c., and also by the spontaneous decomposition of nitrotartaric acid. Sodium bisulphite converts it into glyoxal, while with hydroxylamine it forms the dioxime

corresponding with the diketonic form. With phenylhydrazine-sulphonic acid, it forms *tartrazine*, a beautiful yellow colouring-matter largely used in dyeing wool and silk.

Of the higher ketonic acids the following may be mentioned: *hydrochelidonic acid* (*acetonediacetic acid*), $CO(CH_2\cdot CH_2\cdot CO_2H)_2$; *diacetosuccinic acid*, $\begin{array}{l} CH_3\cdot CO\cdot CH\cdot CO_2H \\ \quad\quad\quad\quad | \\ CH_3\cdot CO\cdot CH\cdot CO_2H \end{array}$; and *diacetylglutaric acid*, $CH_2{<}\begin{array}{l} CH(CO\cdot CH_3)\cdot CO_2H \\ CH(CO\cdot CH_3)\cdot CO_2H \end{array}$ the esters of which give rise to tetrahydrobenzene derivatives or, in presence of ammonia, to pyridine derivatives.

G. POLYVALENT TRIBASIC HYDROXY-ACIDS

ETHANETRICARBOXYLIC ACID, $CO_2H\cdot CH_2\cdot CH(CO_2H)_2$, and ASYM. PROPANETRICARBOXYLIC ACID, $CO_2H\cdot CH_2\cdot CH_2\cdot CH(CO_2H)_2$. These two acids are stable in the form of esters, but in the free state they readily decompose, liberating CO_2 and forming dibasic acids.

TRICARBALLYLIC ACID (Symm. Propanetricarboxylic or Pentadioic-3-methyloic Acid), $CO_2H\cdot CH_2\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$, melts at 163° and is very soluble in water.

It is found in unripe beets and occurs abundantly in the deposits of the vacuum pans of sugar factories. Synthetically it is obtained from *aconitic acid*[1] by the addition of hydrogen and from citric acid, which loses its hydroxyl group when treated with hydriodic acid.

Its constitution is shown by its synthesis from glycerol by way of the tribromhydrin and tricyanohydrin, $C_3H_5(CN)_3$, the latter being hydrolysed.

CITRIC ACID, $\begin{array}{l} CH_2\cdot CO_2H \\ | \\ C{<}\begin{array}{l} OH \\ CO_2H \end{array} \\ | \\ CH_2\cdot CO_2H \end{array}$

This acid is deposited from its aqueous solutions—if these are not too hot—in large, rhombic prisms containing $1H_2O$, which is given up partly in dry air and completely at 130°. It melts at 153° and at a higher temperature decomposes into aconitic and itaconic acids, citraconic anhydride, CO_2, and acetone. It is readily soluble in water (135 : 100 at 15° and 200 : 100 at the boiling-point) or alcohol (53 : 100 at 15° and about double as much in 80 per cent. alcohol), and to a slight extent in ether (9 : 100). It was discovered by Scheele in 1784 and studied by Liebig in 1838. It occurs abundantly in nature in the lemon (4·5 per cent. in the unripe lemon), orange, gooseberry, and other fruits, and in small quantities in cows' milk, the shoots and leaves of the vine, tobacco, and fungi, and as calcium salt in the beet, willow, &c.

Industrially it is obtained by the lime method described later (*see* p. 349). Synthetically it may be prepared from acetonedicarboxylic acid by the action of hydrocyanic acid and subsequent hydrolysis. The constitution thus indicated is confirmed by its formation from symm. dichlorhydrin, $CH_2Cl\cdot CH(OH)\cdot CH_2Cl$, which on oxidation gives symm. dichloracetone,

[1] Aconitic Acid is the corresponding unsaturated acid, $\begin{array}{l} CH\cdot CO_2H \\ \| \\ C\cdot CO_2H \\ | \\ CH_2\cdot CO_2H \end{array}$. It melts at 191°, and is readily soluble in water; it is an energetic acid and is converted into tricarballylic acid by nascent hydrogen. It is prepared by heating dry citric acid, which loses a molecule of water.

It occurs naturally in the sugar-cane, beet, *Aconitum napellus*, &c.

and hence by the introduction of cyanogen groups and hydrolysis yields citric acid:

$$
\begin{array}{c}
CH_2Cl \\
| \\
CO \\
| \\
CH_2Cl
\end{array}
\longrightarrow
\begin{array}{l}
CH_2Cl \\
| \\
C{<}^{OH}_{CN} \\
| \\
CH_2Cl
\end{array}
\longrightarrow
\begin{array}{l}
CH_2Cl \\
| \\
C{<}^{OH}_{CO_2H} \\
| \\
CH_2Cl
\end{array}
\longrightarrow
\begin{array}{l}
CH_2\cdot CN \\
| \\
C{<}^{OH}_{CO_2H} \\
| \\
CH_2\cdot CN
\end{array}
\longrightarrow
\begin{array}{l}
CH_2\cdot CO_2H \\
| \\
C{<}^{OH}_{CO_2H} \\
| \\
CH_2\cdot CO_2H
\end{array}
$$

Citric acid was prepared some years ago (Fabrique de produits chimiques de Thann et de Mulhouse) by Wehmer's biological process (Ger. Pat. 72,957 of 1893), according to which glucose is fermented by certain moulds (*Citromyces Pfefferianus* and *Glaber*, and *Mucor pyriformis*), the yield being about 55 per cent. of the sugar. In 1909 E. Buchner and H. Wüstenfeld studied the most favourable conditions for the development of *Citromyces citricus*, but arrived at no practical results.

When heated for a long time with water, citric acid forms a little aconitic acid, into which it is transformed completely by concentrated hydrochloric acid. It is readily oxidised to acetone, oxalic acid, and carbon dioxide.

Like tartaric acid, citric acid hinders the precipitation of the metallic hydroxides from their salts by ammonia.[1]

Citric acid is used in large quantities for lemonade and in pharmacy and for effervescent drinks (citrate of magnesia); it is employed also in dyeing, analysis, &c. In normal seasons, the price is about £14 per quintal.

SALTS OF CITRIC ACID. Being tribasic, this acid forms three series of salts, as well as two different monosubstituted acids and two disubstituted acids. The alkali salts are all soluble in water, almost all of the others being insoluble, although dissolving in alkali citrates owing to the formation of double salts; in such solutions, the metals are no longer precipitable by ammonia, phosphates, or alkali carbonates. When heated, many citrates give salts of aconitic acid.

CALCIUM CITRATE, $(C_6H_5O_7)_2Ca_3 + 4H_2O$. If calcium hydroxide is added to a dilute solution of citric acid, no precipitate forms in the *cold* but one separates in the hot. In presence of ammonia, calcium chloride gives no precipitate in the cold, while that formed in the hot partly dissolves on cooling but does not dissolve in caustic soda, and so differs from calcium tartrate (*see* p. 336). In moderately concentrated solutions, calcium chloride precipitates calcium citrate, although incompletely, even in the cold; in the hot, precipitation is complete. The water of crystallisation is wholly expelled at about 200°.

Calcium citrate is soluble in ammonium citrate with formation of a double salt precipitable by alcohol.

The manufacture and statistics of calcium citrate are considered later.

BARIUM CITRATE is less soluble in cold water than the calcium salt.

MAGNESIUM CITRATE, $(C_6H_5O_7)_2Mg_3$, is formed by dissolving magnesium carbonate in citric acid solution. It is used as a purgative and is then prepared by heating a mixture of 105 parts of powdered citric acid with 30 parts of magnesium oxide cautiously at 100° to 105°, pouring the fused mass on to porcelain tiles and powdering when cold. Large quantities of *effervescent magnesia* are prepared nowadays as a purgative and refreshing drink by mixing magnesium citrate with sodium bicarbonate and small proportions of citric acid and sugar, and granulating the mass with addition of a little glucose.

[1] **Tests and Reactions for Citric Acid.** *Denigès' reaction* is characteristic and serves to detect small quantities of the acid: the solution is heated to boiling with one-twentieth of its volume of *Denigès' reagent* (5 grms. of mercuric oxide, 80 c.c. of water, and 20 c.c. of concentrated sulphuric acid), 3 to 10 drops of an approximately decinormal potassium permanganate solution being added; a white, crystalline precipitate is formed immediately even with traces of citric acid. The reaction is not masked by the presence of tartaric, oxalic, malic, sulphuric, or phosphoric acid, although the amount of permanganate used must then be slightly increased.

The presence of tartaric acid—which is a common adulterant—in citric acid may be detected by the addition of potassium acetate, the acid potassium citrate thus formed being readily soluble, whilst acid potassium tartrate is only slightly soluble. Minimal quantities of tartaric acid may be also detected as follows: 1 grm. of the powdered substance is heated for a few minutes on the water-bath with 1 c.c. of 20 c.c. ammonium molybdate solution and a few drops of 0·25 per cent. hydrogen peroxide solution; in presence of even 0·001 grm. of tartaric acid, a bluish coloration is obtained. The presence of oxalic acid is easily discovered, since *in the cold* and in an ammoniacal solution calcium oxalate is insoluble, whilst calcium citrate is soluble.

Citric acid and, to some extent, magnesium citrate are often adulterated with tartaric acid, which is cheaper.

CITRATE OF IRON is obtained as a dark red colloidal solution by dissolving ferric hydroxide in cold citric acid solution. Such solutions of different concentrations give, on heating, various citrates of iron which are soluble in ammonium citrate and more or less soluble in water, and have been studied in recent years in relation to their colloidal character.

CITRUS INDUSTRY

Citric acid is manufactured from the juice of lemons yielded especially by the following three plant species: *Citrus limonium*, *Citrus bergamia* (*bergamot*), and *Citrus limetta* (or wild lemon cultivated by the English in Guiana and the East Indies). Lemons are cultivated most extensively in Sicily and Calabria and to a considerable extent also in Spain. The cultivation is of little importance in Greece, the Sandwich Islands, and the East Indies, but is rapidly increasing in Australia. During recent years the production of oranges and lemons has made rapid strides in California and in Florida,[1] where it is already about double that of Sicily. It is pleasing to note that plantations of oranges alone are being more and more largely replaced by those of lemons.

Only the refuse lemons (one-fourth of the total production) are used for the manufacture of citric acid, as they cost only half as much as the picked fruit.

The first operation to which the lemons are subjected is peeling, a workman removing the peel with three cuts of a knife, cutting the lemon in two and throwing it into a tub; the peel is collected separately for the preparation of essence. A skilled operative can peel more than 4000 lemons a day. From 8000 lemons, pressed in a suitable press, 600 litres of juice, containing 4·5 to 6 per cent. of citric acid, are obtained; only 9 to 10 per cent. of the total acid exists as calcium citrate.[2] The juice does not keep well

[1] The lemon orchards in Sicily are found especially on the coast from Palermo to Cefalu (about one-fifth of the total production of lemons and oranges) and on the coast near Messina (more than double that of Palermo–Cefalu), usually on irrigated lands, but sometimes in cool non-irrigated districts. The stocks are obtained from the seed of the wild orange (called by the Sicilians *arancio agro*, or sour orange). The plants from these seeds are planted out in the orchards in their third year and are placed from 3 to 5 metres apart, according to the nature of the soil, to the wind, and to custom. After a year the stock is grafted from an adult plant. Fructification occurs after a further three years and reaches its maximum in ten years. The flowering of the lemons on the same plant is progressive and lasts the whole of May; from the latter half of June to the beginning of October the plants are watered every fortnight. The maturation of the fruit is gradual from November to the end of April and the harvest is gathered in three periods, the best fruit being those of the middle one—December to February; the last fruit, plucked in April and the beginning of May, are poorer in juice and thicker in the peel. In the coast district of Messina, the harvest finishes at the beginning of March.

Lemons have also been forced in Sicily during the past few years, the highly valued summer fruit being thus obtained; these are called *verdelli* (high quality) and *bianchetti* (lower quality). In this case the plants are not watered during June and July, the leaves withering and all the young fruit falling. In August, water in abundance is given at intervals, and sodium nitrate applied as fertiliser. The plant then suddenly becomes very vigorous, and in a few days is covered with new flowers, the fruit ripening rapidly from the end of May to the close of the summer, and that gathered in June or July being of the highest quality. Such plants give an increased crop, especially if manured, and the fruit commands more than double the ordinary prices. This procedure is followed in orchards where the soil is not moist and can be left to dry completely and where the lemons are not alternated with oranges or other crops requiring watering.

Under favourable conditions, a good lemon plant should yield on an average 1000 lemons a year (some very large plants give several thousands). The price varies considerably, 8*s.* to 16*s.* per 1000 being paid for the fruit on the tree and as much as 24*s.* for the gathered fruit; forced lemons cost at least 20*s.* per 1000, the price in 1907 exceeding 40*s.* The cost of gathering, packing, and freight to the port varies from 1*s.* 7*d* to 3*s.* 2*d.* per 1000. The *refuse lemons*, which form about one-fourth of the crop (or more if the demand for lemons is small), cost about half as much as the other fruit (5*s.* to 6*s* per 1000 on the average), although on rare occasions the price reaches 8*s*, and in 1908, at the height of the crisis, it fell to 2*s* per 1000.

[2] *Fresh lemon juice* contains also 7 to 9 per cent. of glucose, 0·2 to 0·8 per cent. of saccharose (according as the lemons are sour or ripe), certain extractive, gummy, and pectic substances (about 0·2 per cent. for ripe and 0·8 per cent for unripe fruit), and about 0·5 to 0·7 per cent. of inorganic salts. The presence of these substances renders it impossible to crystallise the citric acid merely by concentrating the juice, even when all the glucose is transformed into alcohol (5 to 6 per cent). So that, even at the present time, the citric acid is separated by Scheele's classical and rather costly process, according to which it is first converted into calcium citrate. The high price of fuel has prevented the establishment of the citric acid industry in Sicily, and the preparation of the acid has been monopolised for a long time by England and, at the present time, largely by Germany. Both these countries receive the raw material from Sicily, to a small extent as lemons packed in barrels containing sea-water, partly as concentrated juice (*agro cotto*), but mostly as calcium citrate.

In consequence of the development of lemon-growing in Spain, and especially in California and Australia, and also owing to an agreement entered into by the manufacturers of citric acid, the condition of the Sicilian growers became so critical that in 1903 the Italian Minister of Agriculture offered a prize of £6000 for improvements in the industry or new processes of value to the cultivators. This sum was largely wasted by Commissions who achieved nothing or by rewarding certain favoured individuals. However, at the end of 1904, Professor Restuccia, of Messina, announced to the Government the discovery of a process for the direct extraction of citric acid by simple concentration of the juice, to which was previously added a trace of a substance—the nature of

(better if pasteurised at 63° to 65°), and is usually concentrated at once in open pans with direct-fire heating until the specific gravity reaches 60° on the citrometer (1·2394, or 28° Bé.), and the product represents a blackish decoction containing 300 to 400 grms. of citric acid per litre (that from the bergamot of Calabria and Messina contains 300 grms., while that produced in the Sandwich Islands and in the Republic of Dominica from lemons of the limetta species has a density of 1·32 and contains about 575 grms. of citric acid per litre). The boiling decoction is passed through a cloth and is collected in casks for transport.

The commercial value of the juice (*agro cotto*) depends on the content of citric acid, and is determined either by diluting the juice and titrating with normal caustic soda or by precipitating in the hot as calcium citrate and weighing the latter. This estimation is preceded by a qualitative examination to ascertain if salt has been added to increase the specific gravity (test with silver nitrate in presence of a little nitric acid) or if sulphuric or hydrochloric acid has been added to raise the degree of acidity (test with silver nitrate or barium chloride in presence of a little nitric acid).

In the large modern factories, the juice is treated in almost the same manner as in the manufacture of tartaric acid (see p. 341): into 100-hectol. vessels provided with stirrers and cold-water coils are placed 20 hectols. of concentrated juice and 80 hectols. of water, the liquid being then well mixed for thirty minutes and allowed to ferment, the glucose being thus converted into alcohol and the juice clarified. By passing very cold water through the coil the temperature of the liquid is lowered to 5°, and a large part of the dissolved and suspended extractive and mucilaginous matters separated; in presence of a little tannin, these matters coagulate and do not redissolve (50 litres of sumach extract at 10° Bé. are sufficient, the liquid being stirred for 15 to 20 minutes immediately after the addition). The solution is then passed to the filter-presses and thence into 20-hectol. wooden vats or into brickwork vessels similar to the preceding ones, but provided with perforated coils for direct-steam heating. The boiling liquid is now neutralised exactly with dense milk of lime or with powdered calcium carbonate. The latter causes frothing and sometimes overflow of the liquid, but precipitates a purer calcium citrate, the hydroxide throwing down many pectic and colouring matters. For every 100 kilos of citric acid present (titrated) 45 kilos of quicklime (57 of slaked lime or 80 of the carbonate) are added. After stirring while hot, the insoluble tricalcic citrate —which forms immediately—is passed at once through the filter-presses and washed with very hot water for ten minutes, with tepid water for ten minutes, and with cold water for five minutes. In Sicily, *calcium citrate* is prepared in a primitive method (with slaked lime often containing magnesia, which yields soluble magnesium citrate, this being lost) and is sold dry with a content of 64 per cent. of citric acid. 300 kilos of calcium citrate of this strength require, on the average, 100,000 lemons, the peel of which yields 37 kilos of essence selling at 6*s*. 4*d*. per kilo. The total cost of manufacturing calcium citrate and essence from 100,000 lemons is about £10. The cakes of calcium citrate from the filter-presses are mixed in a 20-hectol. lead-lined vessel with 15 hectols. of cold

which he did not reveal (picric acid!)—and a little animal charcoal But this process only led to further waste of money.

In 1910, Peratoner and Scarlata suggested the following new process for extracting the essence and citric acid from the lemons directly, without conversion of the acid into the calcium salt. The juice obtained by squeezing the minced lemons in hydraulic presses is partly distilled in a vacuum on a water-bath at 60° to recover the essence and then concentrated *in vacuo* at 70° until it acquires a syrupy consistency (one-tenth of the original weight). When the syrup is cold, all the citric acid is extracted by treatment with a mixture of alcohol and ether, in which many of the impurities are insoluble. The alcohol and ether are recovered by distillation, and the residue diluted with a little water, filtered, and concentrated *in vacuo*; after standing for twelve to twenty-four hours it sets to a yellowish red crystalline mass which, after defecation and decolorisation in the ordinary way (animal charcoal, &c.), gives pure colourless crystals, the yield being 60 to 70 per cent. The remaining acid can be separated from the mother-liquor as citrate.

In spite of the favourable opinion expressed by Professors Garelli and Paternò, this process does not seem to have been applied practically.

Meanwhile the crisis in the industry, which had apparently lessened as a result of the good crops and prices of 1906 and 1907, became aggravated in 1908 owing to the diminished demand for lemons, to the American crisis, to the agreement between the producers of citric acid to limit the amount of raw material required—thus lowering prices and exhausting the usual stocks of treated products—and, finally, to the abundant production, since refuse lemons did not sell for 2*s*. 6*d* per 1000 at the beginning of 1908 and did not pay for gathering.

Various measures have been taken by the Italian Government to protect the citric acid industry in Sicily, but it should be possible, in the present advanced condition of technical chemistry, to develop this industry without such aid. The sulphuric acid required is now made in Sicily itself, and by the use of multiple-effect evaporating plant, the consumption of coal may be reduced to a minimum. In 1911 a large citric acid factory was erected in the vicinity of Palermo by the firm of Goldenberg, from Winckel, near Wiesbaden (*see later*).

water, the lime of the citrate being then neutralised exactly with dilute sulphuric acid (1 : 5) (with 100 kilos of citric acid in the juice correspond 400 kilos of this dilute acid); a slight excess of sulphuric acid is always added, since the presence of unaltered calcium citrate would hinder the crystallisation of the citric acid.

The acid is added in portions at the rate of 5 litres per minute, the liquid being kept well mixed and direct steam applied through a perforated leaden coil. The mass is boiled for ten to fifteen minutes, the steam then suspended and the whole mixed for thirty minutes. The calcium sulphate is then removed by means of a filter-press and is washed with 200 litres of boiling water, which is added to the first filtrate, and then with cold water, which is afterwards used for treating fresh calcium citrate. The citric acid solutions from the filter-presses contain only minimal quantities of sulphuric acid and certain blackish extractive matters. Concentration of the solution was formerly carried out in lead-lined wooden vessels, 4 metres long, 2 metres wide, and 25 cm. deep, containing closed steam coils. Evaporation should be rapid and the temperature should never exceed 65° to 70°. When the liquid reaches 46° (sp. gr. 1·3), almost all the calcium sulphate previously remaining in solution separates; the clear liquid is then siphoned into a similar vessel underneath, the concentration being continued until a crystalline skin forms at the surface of the liquid, which is next transferred to wooden crystallising vessels, 2 metres × 70 cm. × 20 cm. (deep); the inner surface is polished with plumbago. After two days, the dark brown mother-liquors are removed and the yellowish brown crystals centrifuged. In order to separate traces of dissolved iron from the mother-liquor, this is treated with a little potassium ferrocyanide and filtered; two or three further crops of dark-coloured crystals are obtained, the very dark mother-liquor finally obtained being added to fresh lemon-juice.

In modern factories the citric acid solution, freed from calcium sulphate by filter-pressing, is concentrated in vacuum apparatus, just as in the sugar and tartaric acid industries. In this way, the temperature does not exceed 60° to 65° and with a triple-effect apparatus, not only rapidity but also economy of fuel is attained (*see* vol. i, p. 442, and also section on Sugar).

The brown crystals first obtained are refined and decolorised by dissolving them in rather more than double their weight of water and boiling the solution with animal charcoal previously treated with hydrochloric acid and with other substances, as already mentioned in considering the refining of tartaric acid (p. 342).

In all the washing and refining operations, pure water with little hardness is always employed.

STATISTICS AND PRICES. The production of oranges, lemons, &c., in Italy (Calabria and Sicily) is as follows:

In the five years	1891–1895,	2·60 thousand millions of fruit per annum
,, ,, ,,	1896–1900,	3·72 ,, ,, ,, ,, ,,
,, ,, ,,	1901–1905,	5 ,, ,, ,, ,, ,,
,, year	1907[1]	6 ,, ,, ,, ,, ,,

In 1909, Italy exported 1,109,000 quintals of oranges and 2,560,600 quintals of lemons (£920,000), and in 1910, 1,204,300 quintals of oranges (£481,720) and 2,670,000 of lemons (£929,840).

Sicily exported:

14,428 quintals of *agro cotto*, value	£36,360	in 1903
21,448 ,, ,, ,, ,,	£54,050	,, 1904
12,000 ,, ,, ,, ,,	£35,520	,, 1905
6,000 ,, ,, ,, ,,	£18,000	,, 1907
7,500 ,, ,, ,, ,,	£22,000	,, 1908
1,000 ,, ,, ,, ,,	£3,200	,, 1909

As the exportation of *agro cotto* diminished, that of *calcium citrate* (in casks called *pipes*, holding 305 kilos) increased as follows:

[1] While in other years the picked lemons for use as fruit sold for 12*s*. or even 16*s*. per 1000 (*i.e.* 1½ *cantaros* = about 125 kilos), and the forced fruit for as much as 32*s*, the quotations in July 1908 were as follow: ripe lemons (gathered in winter and spring), 5*s*. 4*d*. to 8*s*. per 1000; verdelli, 17*s*. 6*d* to 20*s*.; bianchetti, 8*s*. to 10*s*.; for pressing, 2*s*. to 2*s*. 4*d*.

1903	..	32,793 quintals, value £135,160 ;	mean price,	92s. per quintal
1904	..	54,310 „ „ £221,240 ;	„ „	100s. „ „
1905	..	41,259 „ „ £181,520 ;	„ „	108s. „ „
1906	..	51,498 „ „ £227,800 ;	„ „	136s. „ „
1907	..	61,684 „ „ £444,120 ;	„ „	160s. „ „
1908	..	77,101 „ „ £400,920 ;	„ „	120s. „ „
1909	..	23,800 „ „ £123,808 ;	„ „	100s. „ „
1910	..	64,755 „ „ £414,400 ;	„ „	127s. „ „

In 1909, on account of the crisis in the industry, exportation diminished considerably, and the price fell as low as 81*s.* 6*d.* per quintal.

The *calcium citrate* [1] exported went to the following countries :

	1905	1906	1907	1908	1909	1910
	Quintals	Quintals	Quintals	Quintals	Quintals	Quintals
Austria-Hungary . .	1,900	600	1,340	3,371	701	2,142
Belgium . . .	2,400	2,600	3,930	2,678	560	1,723
France. . . .	10,000	15,300	20,700	20,915	6,874	14,203
Germany . . .	1,200	1,900	2,150	2,854	508	2,125
England . . .	8,800	9,400	10,000	12,877	3,834	13,097
United States . .	15,600	21,000	21,400	24,147	10,400	24,488

In 1903, 281 works in Calabria and Sicily for the preparation of *agro cotto* employed a total of 4000 workmen and 240 h.p.

The annual production of refined citric acid in Europe varies from 35,000 to 40,000 quintals and the price from 216*s.* to 280*s.* per quintal. In general the price rises and falls with that of tartaric acid, the difference between the prices of the two acids being due to the different degrees of acidity (3 carboxyls in one case and 2 in the other) and molecular weights (152 and 192).

In 1897	Germany imported	2350 quintals	and exported	1070 quintals
„ 1902	„ „	3060 „	„ „	1630 „
„ 1905	„ „	— „	„ „	3793 „
„ 1909	„ „	about 1926 „	„ „	3668 „

Germany also imported 3600 quintals of lemon-juice in 1908 and 1700 quintals in 1909.

Italy imported about 1140 quintals (600 from Germany) of citric acid in 1907 ; 1644 in 1908 ; 1437 (£9268) in 1909 ; and 1094 in 1910 ; the exports were only 10 quintals in 1909. The import duty in Italy was formerly 8*s.* per quintal, but was raised in 1909 to £2 to protect a large factory, with £40,000 capital, erected in 1910–1911 near Palermo by the firm of Goldenberg, which also makes sulphuric acid and tartar products. The first certain result of this procedure will be to raise the price of citric acid in Italy by £2 per quintal, while Italian citric acid will be much cheaper in other countries than in Italy.

In Austria there are two citric acid factories, which, in 1906, imported 544 quintals of calcium citrate from Sicily, 1450 from Turkey, and 4356 from Greece. France has two factories, these importing 18,113 quintals of Sicilian calcium citrate in 1906. In Germany there are nine citric acid works and four of pure citrates, 13,180 quintals of Sicilian calcium citrate being imported in 1908. In England there are ten works, almost all in London. The United States have three very large factories which produce more than 10,000 quintals of citric acid and import also a certain quantity from Europe, although

[1] M. Spica (1910) has suggested a simple, rapid, and exact method for the analysis of *calcium citrate*, the content of citric acid being obtained from the volume of carbon monoxide generated when the citrate is heated with concentrated sulphuric acid. 2 grms. of the citrate, moistened in a flask on the water-bath, are treated with 25 c.c of concentrated sulphuric acid. By means of a current of carbon dioxide, all the carbon monoxide is driven into a nitrometer similar to that illustrated in Fig. 16 (p. 40), the carbon dioxide being absorbed in caustic soda. Each c c. of CO at 0° and 760 mm. corresponds with 0 009407 grm. of citric acid, $C_6H_8O_7 + H_2O$; the method cannot be used with citrate adulterated with oxalate or tartrate.

the protective duty is 63*s*. per quintal; calcium citrate, which is all imported, is free from duty.

Of the **HIGHER POLYBASIC HYDROXY-ACIDS** the following may be mentioned: *desoxalic acid*, $CO_2H \cdot CH(OH) \cdot C(OH)(CO_2H)_2$, which forms deliquescent crystals and, on boiling with water, loses CO_2 and gives uvic acid; *hydroxycitric acid* (dihydroxytricarballylic acid), $C_3H_3(OH)_2(CO_2H)_3$, found in the beet; *acetonetricarboxylic acid* and various acids which contain four, five, or even more carboxyl groups and are of synthetic and not of natural origin.

IV. THIO-ACIDS AND THIO-ANHYDRIDES

These may be regarded as acids or anhydrides in which an oxygen atom is replaced by sulphur, as in **THIOACETIC ACID** (Ethanthiolic Acid), $CH_3 \cdot CO \cdot SH$, which is obtained by the action of phosphorus pentasulphide on acetic acid and is a colourless liquid boiling below 100°, giving an odour of acetic acid and hydrogen sulphide; these two compounds are also formed by the action of water on the acid. **ETHANTHIOLTHIOLIC ACID**, $CH_3 \cdot CS \cdot SH$, is a dithio-acid, and **ACETYL SULPHIDE**, $(CH_3 \cdot CO)_2S$, a thio-anhydride. The esters corresponding with these acids, *e.g.* **ETHYL THIOACETATE**, $CH_3 \cdot CO \cdot SC_2H_5$, a liquid boiling unchanged and yielding the acid and mercaptan on hydrolysis, are also known.

V. AMIDO-ACIDS, AMINO-ACIDS, IMIDES, AMIDINES, THIOAMIDES, IMINO-ETHERS, AND ANALOGOUS COMPOUNDS

A. AMIDO-ACIDS (AMIDES) AND DERIVATIVES

Like the amines (*see* p. 200), the amides may be regarded as derivatives of ammonia, the hydrogen atoms of which are replaced, not by alkyl, but by acid radicals.

There are thus *primary*, *secondary*, and *tertiary amides*, which are obtained by the replacement of one, two, or three atoms of hydrogen, and are sharply distinguished from the amines, as they are readily hydrolysed by alkali, acid, or superheated water, giving ammonia and the corresponding acids. They are generally crystalline substances soluble in alcohol or ether, and the lower members, especially of the primary amides, dissolve also in water. Their boiling-points are much higher than those of the corresponding amines.

Amides are also known in which one or two atoms of the ammoniacal hydrogen are replaced by alkyl radicals, *i.e. alkylated amides*, *e.g. ethylacetamide* or *acetylethylamine*, $CH_3 \cdot CO \cdot NH \cdot C_2H_5$, and *dimethylacetamide*, $CH_3 \cdot CO \cdot N(CH_3)_2$, from which, on hydrolysis, only the acid is separated, the alkyl residue or residues remaining joined to the amino-group, forming non-hydrolysable amines.

PREPARATION. (1) By dissolving an alkyl cyanide (nitrile) in concentrated sulphuric acid, either with or without concentrated acetic acid, concentrated hydrochloric acid or hydrogen peroxide, a molecule of water is added: $CH_3 \cdot CN + H_2O = CH_3 \cdot CO \cdot NH_2$. By heating acids or anhydrides with nitriles, secondary or tertiary amides are formed.

(2) The action of ammonia solution or solid ammonium carbonate on acid chlorides yields primary amides, whilst, if the ammonia is replaced by an amine, an alkylated amide is obtained:

$$CH_3 \cdot CO \cdot Cl + 2NH_3 = NH_4Cl + CH_3 \cdot CO \cdot NH_2$$

$$CH_3 \cdot CO \cdot Cl + 2NH_2 \cdot C_2H_5 = \underset{\text{Ethylamine hydrochloride}}{C_2H_5 \cdot NH_2, HCl} + \underset{\text{Ethylacetamide}}{CH_3 \cdot CO \cdot NH \cdot C_2H_5}.$$

On the other hand, the anhydrides give, with ammonia, the primary anhydride and an ammonium salt.

(3) By heating ammonium salts of the fatty acids in closed vessels at about 250°, primary amides are formed :

$$CH_3 \cdot CO_2NH_4 = H_2O + CH_3 \cdot CO \cdot NH_2.$$

Properties. Unlike the amines, the amides have only a very feeble basic character, owing to the presence of the negative acid radical, and only the primary ones give additive products with acids, *e.g.* $CH_3 \cdot CO \cdot NH_2$, HCl, acetamide hydrochloride, which is decomposed even by water. Also certain sodium and mercuric derivatives are known, *e.g.* $(CH_3 \cdot CO \cdot NH)_2Hg$, which exhibit the amides as feebly acid compounds, one of the hydrogen atoms of the amido-group being replaceable by metals.

With nitrous acid, amides react similarly to primary amines, giving the acid and liberating nitrogen :

$$CH_3 \cdot CO \cdot NH_2 + NO_2H = H_2O + N_2 + CH_3 \cdot CO_2H.$$

Removal of water from primary amides by means of phosphorus pentachloride or pentoxide results in the formation of alkyl cyanides (nitriles).

By the gradual action of bromine in presence of alkali, the corresponding amine with one less carbon atom is finally obtained, while urea derivatives, such as *methylacetylurea*, $CO{<}{}^{NH \cdot COCH_3}_{NH \cdot CH_3}$, are formed as intermediate products, these being decomposable by excess of alkali ; an intermediate bromo-compound, *e.g.* *acetobromamide*, $CH_3 \cdot CO \cdot NHBr$, is also formed, this giving the amine with liberation of CO_2 :

$$CH_3 \cdot CO \cdot NHBr + KOH = KBr + CO_2 + CH_3 \cdot NH_2$$

When, however, the acid residue contains more than five carbon atoms, the nitrile is obtained instead of the amine, which is acted on by the bromine : $C_nH_{2n+1} \cdot CH_2 \cdot NBr_2 = 2HBr + C_nH_{2n+1} \cdot CN$. Since the nitriles can be converted into the acids containing one less carbon atom than the amides from which they originate, it is hence possible *to pass gradually from higher acids to more and more simple ones.*

The ready hydrolysability and the methods of formation of amides confirm their constitutional formula, $X \cdot CO \cdot NH_2$. But with the alkali salts, the existence of the isomeric modification, $X \cdot C(OH) : NH$ (*see* Tautomerism, pp. 17 and 330) is assumed, but if the hydrogen of the hydroxyl or amino-group is replaced by an alkyl residue, no tautomeric forms occur, only true structural isomerides, $X \cdot CO \cdot NHR$ and $X \cdot C(OR) : NH$. The latter are termed *imino-ethers* and are derived from the hypothetical imino-hydroxides of the acids, *e.g.* $CH_3 \cdot C(OH) : NH$. They are prepared by the action of a nitrile on an alcohol in presence of gaseous hydrogen chloride ; thus, with HCN, the *hydrochloride of formiminic ether*, $CH(OC_2H_5) : NH$, is obtained as a white powder.

It is worthy of mention that Effront decomposes amino-acids on an industrial scale by means of special ferments so as to obtain fatty acids and ammonia from them (*see* pp. 155 and 288).

FORMAMIDE (Methanamide), $H \cdot CO \cdot NH_2$, prepared as described above, is a liquid which is soluble in water and alcohol, boils at 200° with partial decomposition, and gives ammonia and carbon monoxide when rapidly heated ; with P_2O_5 it yields HCN, and with chloral, an additive product, *chloralamide*, which is used as an antiseptic and hypnotic.

ACETAMIDE (Ethanamide), $CH_3 \cdot CO \cdot NH_2$, forms needles melting at 82° and boils at 222°. *Diacetamide*, $(CH_3 \cdot CO)_2NH$, melts at 78°, boils at 223°, and is obtained by heating acetamide with acetic anhydride.

OXAMIC ACID, $CO_2H \cdot CO \cdot NH_2$, is the monamide of oxalic acid and is obtained as a white, crystalline powder, slightly soluble in cold water, when ammonium oxalate is heated.

OXAMIDE, $NH_2 \cdot CO \cdot CO \cdot NH_2$, is the diamide or normal amide of oxalic acid, and is obtained by the partial hydrolysis of cyanogen or by distillation of ammonium oxalate. In appearance it closely resembles oxamic acid and it is insoluble in water or alcohol and is readily hydrolysed ; elimination of water (by P_2O_5) from it leads to cyanogen.

SUCCINAMIC ACID, $CO_2H \cdot CH_2 \cdot CH_2 \cdot CO \cdot NH_2$, is analogous to oxamic acid, and succinamide, $NH_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO \cdot NH_2$, is prepared similarly to oxamide, to which it is analogous ; succinamide crystallises from water in shining needles, and decomposes at 200° into ammonia and succinimide.

Of the *amides of hydroxy-acids*, only the following need be mentioned :

GLYCOLLAMIDE, $OH \cdot CH_2 \cdot CO \cdot NH_2$, which is obtained by treating the ester of glycollic acid with ammonia or, better, by heating ammonium tartronate at 150°, melts at 120° and has a sweet taste. The *diglycollamides*, $NH_2 \cdot CO \cdot CH_2 \cdot O \cdot CH_2 \cdot CO_2H$ and $(CH_2 \cdot CO \cdot NH_2)_2O$, are also known, the latter, on heating, giving ammonia and *diglycollimide*, $O{<}{\scriptstyle CH_2 \cdot CO \atop CH_2 \cdot CO}{>}NH$, which melts at 142°.

MALIC ACID, $CO_2H \cdot CH_2 \cdot CH(OH) \cdot CO_2H$, forms two amides by means of its two carboxyl groups, an amine by means of its alcoholic group (aspartic acid), and also an amino-amide (asparagine).

MALAMIC ACID, $NH_2 \cdot CO \cdot CH_2 \cdot CH(OH) \cdot CO_2H$, is known best as its crystalline ethyl ester, which is formed by the action of ammonia on an alcoholic solution of ethyl malonate.

MALAMIDE, $NH_2 \cdot CO \cdot CH_2 \cdot CH(OH) \cdot CO \cdot NH_2$, is formed by the action of ammonia on ethyl malonate in the dry state.

B. IMIDES AND IMINO-ETHERS

Attention must be drawn, not so much to the secondary amides (in which two hydrogen atoms of ammonia are replaced by two acid residues, *as in diacetamide*, $(CH_3 \cdot CO)_2NH$, which contains the iminic group, NH) or to the tautomeric form of the primary amides (with $X \cdot C{\scriptstyle {/\!\!/ O} \atop {\backslash NH_2}}$ corresponds the isomeride $X \cdot C{\scriptstyle {/ OH} \atop {\backslash\!\!\backslash NH}}$, which is well known in the form of *imino-ethers*, $X \cdot C{\scriptstyle {/ OR} \atop {\backslash\!\!\backslash NH}}$, or, in the case of the *imidohydrin of glycollic acid*, $OH \cdot CH_2 \cdot C{\scriptstyle {/ OH} \atop {\backslash\!\!\backslash NH}}$; in the free state) as to the imides of certain dibasic acids.

OXIMIDE, $\begin{matrix} CO \\ | \\ CO \end{matrix}{>}NH$ (perhaps with the double formula), is formed on elimination of water from oxamic acid (by PCl_5).

SUCCINIMIDE, $\begin{matrix} CH_2 \cdot CO \\ | \\ CH_2 \cdot CO \end{matrix}{>}NH$, is obtained by heating succinic anhydride in a current of ammonia or by heating the diamide or rapidly distilling mono-ammonium succinate, as has been mentioned on p. 306, where the reason was given for the ready formation of the closed-ring internal anhydrides.

Succinimide melts at 126° and boils at 288°, crystallises with $1H_2O$ and *exhibits the characters of an acid*, the iminic hydrogen, influenced by the two carboxyl groups, being replaceable by acids. On the other hand, when they are treated with alkali, these imides gives the amides from which they originate, a molecule of water being added : $\begin{matrix} CH_2 \cdot CO \\ | \\ CH_2 \cdot CO \end{matrix}{>}NH + H_2O = \begin{matrix} CH_2 \cdot CO_2H \\ | \\ CH_2 \cdot CO \cdot NH_2 \end{matrix}$.

It is interesting that, when succinimide is distilled over zinc dust, it yields

pyrrole, $\begin{array}{l} CH:CH \\ | \\ CH:CH \end{array}\!\!>\!NH$, while, if it is heated in alcoholic solution with sodium (reduction), it gives Pyrrolidine, $\begin{array}{l} CH_2\cdot CH_2 \\ | \\ CH_2\cdot CH_2 \end{array}\!\!>\!NH$.

Also Phenylsuccinimide (Succinanil), $\begin{array}{l} CH_2\cdot CO \\ | \\ CH_2\cdot CO \end{array}\!\!>\!N\cdot C_6H_5$, is known and its various transformations confirm the symmetry of its own structure and consequently also that of succinimide.

GLUTARIMIDE, $CH_2\!<\!\begin{array}{l} CH_2\cdot CO \\ CH_2\cdot CO \end{array}\!\!>\!NH$, is obtained by distilling ammonium glutarate; it melts at 152° and gives a little pyridine when heated with zinc dust.

C. AMINO-ACIDS AND THEIR DERIVATIVES

In the amino-acids, it is the hydrogen in direct union with carbon that is replaced by the NH_2-group, the carboxyl group remaining intact, so that these compounds have both acidic and basic functions and can hence be readily separated from other substances, since after the carboxyl is esterified, salts such as the hydrochlorides of the amino-group are formed.

These substances and their derivatives are of considerable importance in animal and vegetable physiology, since they are found among the products of the gradual synthesis and decomposition of the proteins in the living organism; they are also of interest theoretically, as they form intermediate products in various chemical syntheses.

The α-amino-acids are readily obtained by the action of ammonia on the cyanohydrins of ketones and aldehydes and hydrolysis of the remaining nitrile group:

$$\underset{\text{Nitrile of lactic acid}}{CH_3\cdot C\!\begin{array}{l} \diagup OH \\ -H \\ \diagdown CN \end{array}} + NH_3 = H_2O + \underset{\text{Nitrile of alanine}}{CH_3\cdot C\!\begin{array}{l} \diagup NH_2 \\ -H \\ \diagdown CN \end{array}}$$

$$CH_3\cdot C\!\begin{array}{l} \diagup NH_2 \\ -H \\ \diagdown CN \end{array} + 2H_2O = NH_3 + \underset{\text{Alanine (}\alpha\text{-Aminopropionic acid)}}{CH_3\cdot C\!\begin{array}{l} \diagup NH_2 \\ -H \\ \diagdown CO_2H \end{array}}$$

They are also formed generally by reducing the oximes of ketonic acids or, better, by the action of ammonia on halogenated acids:

$$CO_2H\cdot CH_2Cl + NH_3 = HCl + CO_2H\cdot CH_2\cdot NH_2.$$

We may also mention the interesting Körner-Menozzi reaction (*see* p. 314), which allowed these authors, by inverting the reaction, to pass from the esters of unsaturated acids (fumaroid or maleinoid form) to a single form of the corresponding saturated amino-acids by simple treatment with ammonia (or even an alkylamine in alcoholic solution).

With nitrous acid, the amino-acids give hydroxy-acids and they give many reactions analogous to those of the hydroxy-acids and varying with the position of the amino-group.

Two molecules of an α-amino-acid readily lose 2 mols. of water, giving a kind of anhydride with an imido-ketonic character:

$$\begin{array}{l} CO_2H\cdot CH_2\cdot NH_2 \\ NH_2\ CH_2\cdot CO_2H \end{array} = 2H_2O + \begin{array}{l} CO\cdot CH_2\cdot NH \\ \vert \qquad\quad\ \vert \\ NH\cdot CH_2\cdot CO \end{array}$$

The γ-amino-acids, however, give internal anhydrides analogous to the lactones and termed **Lactams**:

$$CO_2H\cdot CH_2\cdot CH_2\cdot CH_2\cdot NH_2 = H_2O + \begin{array}{l} CO\cdot CH_2\cdot CH_2\cdot CH_2 \\ \vert \qquad\qquad\qquad\ \ \vert \\ \text{———————}NH \end{array}$$

The β-amino-acids, when heated, evolve ammonia and give unsaturated acids.

GLYCOCOLL (Glycine, Aminoacetic or Aminoethanoic Acid, or Amine of Glycollic Acid), $CO_2H\cdot CH_2\cdot NH_2$, is formed on boiling gelatine with alkali [$Ba(OH)_2$] or acid (dilute H_2SO_4) or on heating *hippuric acid* (benzoylglycocoll) with dilute acid: $CO_2H\cdot CH_2\cdot NH\cdot CO\ C_6H_5 + H_2O = CO_2H\ CH_2\cdot NH_2 + C_6H_5\cdot CO_2H$ (benzoic acid). Synthetically it is obtained from monochloracetic acid and concentrated ammonia (*see* p. 322); if the ammonia is replaced by methylamine, *sarcosine*, $CO_2H\cdot CH_2\cdot NH\cdot CH_3$, m.pt. 115°, is obtained, or if by trimethylamine, betaine (*see* p. 323) is formed:

$$CO_2H\cdot CH_2Cl + N(CH_3)_3 = HCl + \begin{array}{l} CO\cdot CH_2\cdot N(CH_3)_3. \\ \vert \qquad\quad\ \ \vert \\ O\text{————} \end{array}$$

Betaine, $C_5H_{11}O_2N$, crystallises with $1H_2O$, which it loses at 100°, or in a desiccator over sulphuric acid. It dissolves in water or alcohol, from which it is precipitated by ether or as *betaine hydrochloride*, by hydrochloric acid. This solid hydrochloride is soluble in water, which hydrolyses it to a considerable extent, the solution then behaving like hydrochloric acid. Owing to this property it is sold, under the name of *acidol*, in pastilles containing exact and suitable doses for stomach complaints, and replaces solutions of hydrochloric acid for this purpose; the same effect as that of the acid is thus obtained by a solid product. *Betaine* is a feeble base, and is not decomposed even by boiling *aqua regia;* at high temperatures it decomposes, giving trimethylamine. It occurs abundantly in beet-sugar molasses (10 to 12 per cent., besides 1 to 2 per cent. of *leucine* and *isoleucine* and 5 to 7 per cent. of *glutamic acid*), from which it is extracted by means of alcohol; after evaporation of this solvent, it is separated as hydrochloride.

The action of tertiary amines, other than trimethylamine, with monochloracetic acid gives various compounds to which is given the name of **BETAINES.**

Substitution in the amino-group of the amino-acids also yields other interesting compounds, *e.g.* **Aceturic Acid** (*acetylglycocoll*), $CO_2H\cdot CH_2\cdot NH\cdot CO\cdot CH_3$, melting at 206°.

The properties of glycocoll and its salts are given on p. 322.

In the amino-acid group is also found **SERINE** or **α-amino-β-hydroxypropionic acid,** $CO_2H\cdot CH(NH_2)\cdot CH_2\cdot OH$, which is obtained on boiling silk gelatine with dilute sulphuric acid or synthetically from glycollic aldehyde, ammonia, and hydrocyanic acid. **LEUCINE** (**α-aminoisocaproic acid**), $CO_2H\cdot CH(NH_2)\cdot CH_2\cdot CH(CH_3)_2$, is obtained synthetically by hydrolysing the nitrile of isovaleraldehyde-ammonia, and is usually found with glycine among the products of decomposition of the proteins by acid or alkali, and is then optically active (the carbon atom adjacent to the carboxyl being asymmetric).

ASPARTIC ACID (Aminosuccinic Acid), $CO_2H\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$, is one of the most important products obtained by the decomposition of proteins by acid or alkali. It occurs in abundance (lævo-rotatory) in beet-sugar molasses, and has been prepared by various synthetic methods, *e.g.* by the action of ammonia on bromosuccinic acid.

Three stereoisomerides are known, two of them being optically active owing to the presence of an asymmetric carbon atom. They are obtained in small, tabular, dimetric crystals, soluble to some extent in hot water. Their cold solutions and also acid solutions of the dextro-rotatory acid have a sweet

taste, but hot solutions or alkaline solutions of the lævo-rotatory acid are without taste.

They give the general reaction of amines and amides with nitrous acid, being converted into malic acid.[1]

The higher homologue of aspartic acid is Glutamic Acid (*a-aminoglutaric acid*), $CO_2H\cdot CH(NH_2)\cdot CH_2\cdot CH_2\cdot CO_2H$.

Among the **DIAMINO-ACIDS** we have **Lysine**, $CO_2H\cdot CH(NH_2)\cdot [CH_2]_4\cdot NH_2$, which is obtained by the action of acids on proteins or by synthetical methods; on putrefaction it gives pentamethylenediamine.

Ornithine, $CO_2H\cdot CH(NH_2)\cdot [CH_2]_3\cdot NH_2$, is the lower homologue of lysine and gives tetramethylenediamine (*putrescine*) on putrefaction.

Taurine (*Ethyleneaminosulphonic Acid*), $SO_3H\cdot CH_2\cdot CH_2\cdot NH_2$, is found in ox-bile combined with cholic acids as *taurocholic acid* (for properties of taurine, *see* p. 214).

Cysteine (*Thioserine*), $CO_2H\cdot CH(NH_2)\cdot CH_2\cdot SH$, is formed by the reduction of cystine, $CO_2H\cdot CH(NH_2)\cdot CH_2\cdot S\cdot S\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$, which occurs in urinary sediments (calculi).

ASPARAGINE, $NH_2\cdot CO\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$, is the amide of aspartic acid. It was first found in asparagus, but is moderately widespread in almost all vegetables (beet, potatoes, beans, vetches, peas, &c.) during the germination period, and the dry seeds of certain lupins contain as much as 30 per cent. The constitution of asparagine is confirmed by the various syntheses leading to its production.

It crystallises with $1H_2O$ in lævo-hemihedral, trimetric prisms, soluble in hot water but insoluble in alcohol or ether.

With aqueous cupric acetate solution, it forms a blue, well-crystallised copper salt $(C_4H_7O_3N_2)_2Cu$, insoluble in water. It is isomeric with malamide, from which is differs in the possession of both acid and basic characters. It is lævo-rotatory and has an unpleasant, insipid taste, but vetch seedlings contain a dextro-rotatory asparagine which has a sweet taste (Piutti, 1886), but does not unite with the lævo-rotatory form—also present in the seedlings—to give the inactive modification. Pasteur stated that the substance composing the nerves of the palate behaves as an optically active combination which acts differently towards the dextro- and lævo- asparagines.

Asparagine is converted into aspartic acid by hydrolysis and into malic acid by the action of nitrous acid.

ASPARTAMIDE, $NH_2\cdot CO\cdot CH_2\cdot CH(NH_2)\cdot CO\cdot NH_2$, is the diamide or normal amide of aspartic acid.

Numerous higher homologues of aspartic acid (Homo-Aspartic Acids) and of asparagine (Homo-Asparagines) are known.

D. AMIDO- AND IMIDO-CHLORIDES

With both the primary amides and also the alkylated amides, the oxygen is readily replaced by chlorine by the action of PCl_5. Thus, acetamide gives *acetamido-chloride*, $CH_3\cdot CCl_2\cdot NH_2$, and ethylacetamide, *ethylacetamido-chloride*, $CH_3\cdot CCl_2\cdot NH\cdot C_2H_5$. Both of these compounds readily lose HCl, forming *imino-chlorides*, *e.g. acetimino-chloride*, $CH_3\cdot CCl:NH$, and *ethylacetimino-chloride*, $CH_3\cdot CCl:N\cdot C_2H_5$. These imino-chlorides, like amido-chlorides, are readily decomposed by water into hydrogen chloride and amide. These chlorinated compounds react easily with aromatic substances and with hydrogen sulphide, ammonia, and amines, the chlorine being thus replaced by sulphur or by amino-residues, forming *thioamides*, *e.g.* $CH_3\cdot CS\cdot NHX$, and *amidines*, *e.g.* $CH_3\cdot C(NH_2):NX_2$.

[1] By the action of nitrous acid on the ethyl ester of glycocoll, Curtius obtained Ethyl Diazoacetate $\begin{matrix}N\\ \|\\ N\end{matrix}\!\!>\!CH\cdot CO_2C_2H_5$, as a yellow oil with a peculiar odour; when heated with water it explodes, losing nitrogen and taking up water to form ethyl glycollate.

E. THIOAMIDES

These are well-crystallised compounds, more acid in character than the amides, and hence capable of forming metallic derivatives and of dissolving in alkali. Besides by the reaction just mentioned they are obtained by the addition of H_2S to nitriles: $CH_3\cdot CN + H_2S = CH_3\cdot CS\cdot NH_2$ (*thioacetamide* or *ethanethioamide*); on heating, the opposite change occurs.

Phosphorus pentasulphide replaces the oxygen of amides by sulphur, thus forming thioamides. With H_2S, isonitriles give the alkylated thioamides of formic acid, $CN\cdot X + H_2S = H\cdot CS\cdot NHX$.

Thioamides are readily hydrolysed (by alkali, hot water, &c.), with formation of H_2S, NH_3 (or amine), and the corresponding acids:

$$X\cdot CS\cdot NHX' + 2H_2O = X\cdot CO_2H + NH_2X' + H_2S.$$

F. IMINOTHIOETHERS

The thioamides (and especially their derivatives) can exist in the isomeric or tautomeric form, $X\cdot C(SH):NH$, in which the hydrogens of both the sulphydryl and the imino-group are replaceable by alkyl groups, **Iminothioethers**, *e.g.* $X\cdot C(SX'):NH$, being then formed. These are prepared by the action of alkyl iodides on the thioamides (also from thioalcohols, nitriles, and gaseous hydrogen chloride), *e.g.* $CH_3\cdot CS\cdot NH_2 + CH_3I =$ $CH_3\cdot C\begin{cases} S\cdot CH_3 \\ NH \end{cases}$, HI (*acetiminothiomethyl hydriodide*).

The iminothioethers are easily hydrolysed (by HCl), forming ammonia and esters of thio-acids:

$$CH_3\cdot C\begin{cases} S\cdot CH_3 \\ NH \end{cases} + H_2O = NH_3 + CH_3\cdot CO\cdot SCH_3.$$

G. AMIDINES

When the amides or alkylamides are heated with amines in presence of a dehydrating agent (like PCl_5), the oxygen of the amide is substituted by an imino-residue:

$$X\cdot CO\cdot NH_2 + R\cdot NH_2 = H_2O + X\cdot C\begin{cases} NH_2 \\ NR \end{cases}$$

$$X\cdot CO\cdot NHX' + R\cdot NH_2 = H_2O + X\cdot C\begin{cases} NHX' \\ NR \end{cases}$$

These compounds are obtained also from thioamides, isothioamides, iminochlorides, or iminoethers by the action of ammonia or of primary or secondary amines:

$$CH_3\cdot CS\cdot NH_2 + NH_3 = H_2S + CH_3\cdot C\begin{cases} NH \\ NH_2 \end{cases} \text{ (\textit{acetamidine} or \textit{ethanamidine}).}$$

$$X\cdot C\begin{cases} NH \\ SX' \end{cases} + R\cdot NH_2 = X\cdot C\begin{cases} NH \\ NHR \end{cases} + HSX'.$$

When nitriles are heated with the hydrochlorides of primary (of the aromatic series also) or secondary amines (not with NH_4Cl), alkylamidines are obtained:

$$CH_3\cdot CN + R\cdot NH_2 = CH_3\cdot C(:NH)\cdot NHR.$$

Properties. The amidines (or *amimides*) are bases and usually of the aromatic series; they are easily hydrolysed (by boiling with alkali or acid), giving (when the iminic hydrogen

is not replaced by an alkyl group) ammonia (or an amine) and a nitrile ; the same change occurs on dry distillation. With H_2S they give first an additive product :

$$X \cdot C(:NH) \cdot NHX' + H_2S = X \cdot C \begin{cases} NHX' \\ SH \\ NH_2 \end{cases}$$

this product then decomposes in two senses, giving (*a*) $X \cdot CS \cdot NHX' + NH_3$ and (*b*) $X \cdot CS \cdot NH_2 + X' \cdot NH_2$.

With CS_2, amidines give thioamides and, at the same time, thiocyanic acid or an alkyl thiocyanate.

H. HYDRAZIDES AND AZIDES

Introduction of an acid residue into hydrazine, $H_2N \cdot NH_2$ (*see* vol. i, p. 327), gives the *primary hydrazides* or *monoacylhydrazides*, *e.g.* $CH_3 \cdot CO \cdot NH \cdot NH_2$ (*acetylhydrazide*) and $H \cdot CO \cdot NH \cdot NH_2$ (*formhydrazide*, m.pt. 54°) ; two acid radicals give *secondary hydrazides* or *dihydrazides*, *e.g.* $CH_3 \cdot CO \cdot NH \cdot NH \cdot CO \cdot CH_3$ (*diacethydrazide*, which melts at 138° and is prepared from hydrazine hydrate and acetic anhydride).

They are readily hydrolysable, and reduce ammoniacal silver nitrate solution in the cold and Fehling's solution on heating. The primary hydrazides are more highly basic than the amides, and so give more stable salts. Nitrous acid acts on primary hydrazides, forming *azides*, which are derivatives of hydrazoic acid (*see* vol. i, p. 327) :

$$CH_3 \cdot CO \cdot NH \cdot NH_2 + HNO_2 = 2H_2O + CH_3 \cdot CO \cdot N \left\langle \begin{matrix} N \\ \| \\ N \end{matrix} \right.$$

These resemble the acichlorides in many properties, but are explosive and, when heated with alcohol, give urethanes and liberate nitrogen :

$$CH_3 \cdot CO \cdot N \left\langle \begin{matrix} N \\ \| \\ N \end{matrix} \right. + C_2H_5 \cdot OH = N_2 + CH_3 \cdot NH \cdot CO_2C_2H_5, \textit{ methylurethane},$$

which can be hydrolysed with formation of CO_2, alcohol, and methylamine. It is hence possible to pass from an acid to an amine with one carbon atom less, by way of the hydrazide and azide.

I. HYDROXYLAMINE-DERIVATIVES OF ACIDS

Hydroxylamine or its residues can be united to acid residues, forming **Hydroximic** (or *hydroxamic*) **Acids**, *e.g.* $CH_3 \cdot C(:N \cdot OH)OH$ (*ethylhydroxamic acid*, m.pt. 59°), and **Amidoximes**, $X \cdot C(:N \cdot OH) \cdot NH_2$. The hydroxamic acids have an acid character and are formed, with evolution of ammonia, by the action of hydroxylamine on amides.

Also **Formyloxime Chloride**, $CH(:N \cdot OH)Cl$, is known, this being obtained by treating mercury fulminate in the cold with HCl ; it forms needles, which are readily decomposable, volatile, and soluble in ether.

The **Amidoximes** are formed by the addition of nitriles to hydroxylamine, $CH_3CN + NH_2 \cdot OH = CH_3 \cdot C(:NOH)NH_2$. If hydrogen cyanide is employed, **ISURET** (**Methanamidoxime** or **Methenylamidoxime**), $CH(:NOH)NH_2$, isomeric with urea, would be obtained.

VI. CYANOGEN COMPOUNDS

Some cyanogen compounds, especially **Hydrocyanic Acid, HCN, potassium cyanide**, and ferro- and ferricyanides, have already been dealt with in vol. i, pp. 397, 437, and 650. We have to consider here the numerous and varied organic derivatives of cyanogen, which are of some interest as they often exist in polymerised forms and almost always in two isomeric modifications, sharply differentiated by their chemical properties : derivatives of *nitriles*, $X \cdot C \vdots N$, and of *isonitriles*, $C \vdots N \cdot X$ (*see also* p. 199).

CYANOGEN, $(CN)_2$, is a highly poisonous gas with a pungent odour recalling that of bitter almonds ; it is liquid at −21° and solid at −34°. It

is found in the gas from blast-furnaces and occurs largely in the tail of Halley's comet, which approached the earth in May 1910. It is obtained by the elimination of water from ammonium oxalate or oxamide ($NH_2 \cdot CO \cdot CO \cdot NH_2$), by the action of P_2O_5 in the hot, or by heating a solution of copper sulphate with potassium cyanide, and is commonly prepared by heating cyanide of silver or of mercury, $Hg(CN)_2 = Hg + (CN)_2$; as a secondary product, **PARACYANOGEN**, $(C_3N_3)_2$, or $(CN)_x$ is formed as a brown powder.

It burns with a purple flame, dissolves readily in alcohol or water (4 : 1), and its solutions gradually become brown, with formation of oxalic acid, formic acid, hydrocyanic acid, ammonia, and urea, and deposition of **Azulmic Acid** (brown powder). With H_2S it forms the **thioamides** : **RUBEANHYDRIC ACID**, $NH_2 \cdot CS \cdot CS\ NH_2$, and **FLAVEANHYDRIC ACID**, $NC \cdot CS \cdot NH_2$.

CYANOGEN CHLORIDE, $NC\ Cl$, is of importance in the synthesis of many cyanogen compounds, and is formed by the action of chlorine on hydrocyanic acid or metallic cyanides: $NC \cdot H + Cl_2 = HCl + NC \cdot Cl$. It is a colourless gas which is easily liquefied, boils at 15·5°, has a pungent odour, and dissolves in water. In presence of HCl it polymerises, forming **Cyanogen Trichloride** (melts at 145°, boils at 190°). With KOH it forms potassium cyanate, NCOK.

CYANIC ACID, $NC\ OH$, is a liquid of penetrating odour and only slight stability, even at the ordinary temperature.

It is obtained by the dry distillation of cyanuric acid (*q.v.*) and condensation of the vapours in a freezing mixture. It undergoes change, even at the ordinary temperature and with slight explosions, into a compact, white isomeride, which is polymerised *iso-cyanic acid* or *cyamelide* $(O : C : NH)_x$; this, on dry distillation, gives cyanic acid again.

Its salts are more stable, but when attempts are made to liberate the acid from these by the action of mineral acids, immediate hydrolysis occurs:

$$NC \cdot OH + H_2O = CO_2 + NH_3.$$

If it is liberated by dilute acetic acid, the isomeric cyanuric acid is obtained.

The alkyl derivatives of cyanic acid exhibit two isomeric forms: **Cyanates**, $N \vdots C \cdot OX$, and **Isocyanates**, $O : C : NX$.

Potassium Cyanate, NCOK, forms white scales soluble in alcohol or water, and is obtained by oxidising solutions of potassium cyanide by means of potassium permanganate or dichromate, or by fusing potassium cyanide or ferrocyanide with PbO_2 or MnO_2: $NCK + O = NCOK$.

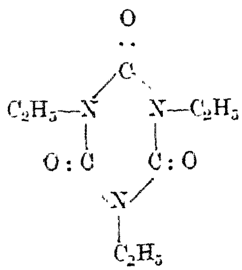
Ammonium Cyanate, $NC \cdot ONH_4$, is isomeric with urea, into which it can be converted. It is obtained by neutralising cyanic acid with ammonia and forms a moderately stable, white, crystalline mass.

ETHYL ISOCYANATE, $CO : NC_2H_5$, is prepared by distilling potassium cyanate with either potassium ethyl sulphate, or ethyl iodide. It is a liquid of penetrating odour and boils at 60°. It does not behave as a true ester (true esters of cyanic acid do not exist), since the action of acid or alkali yields, not alcohol, but ethylamine; $CO : NC_2H_5 + H_2O = CO_2 + C_2H_5 \cdot NH_2$. Hence the nitrogen is united directly to the alkyl group, so that the structure is not $N \vdots C \cdot OC_2H_5$, but $O : C : NC_2H_5$.

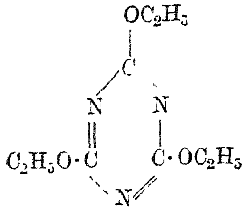
Ethyl isocyanate is instantly decomposed by water, forming derivatives of urea; the latter are also formed by the action of ammonia or amino-bases.

CYANURIC ACID, $(NC)_3(OH)_3$, is a polymeride of cyanic acid and on heating urea —which contains the constituents of ammonia and cyanic acid—either alone or in a current of chlorine so as to eliminate the elements of ammonia, there remain those of cyanic acid, which polymerise to cyanuric acid. It crystallises with $2H_2O$ in prisms, effloresces in the air, and is readily soluble in hot water. When heated with HCl, it hydrolyses slowly to NH_3 and CO_2; with PCl_5 it gives the chloride of cyanuric acid. It is a tribasic acid and forms a violet, crystalline copper salt; its sodium salt is insoluble in concentrated alkalis. Like cyanic acid, it gives rise to two series of derivatives, *e.g.* **Ethyl Cyanurate**, $(NC)_3(OC_2H_5)_3$, which is a colourless liquid giving alcohol on hydrolysis. It is only slightly stable, and is readily transformed into the isomeride of the other series, **Ethyl Isocyanurate**, $(CO)_3(NC_2H_5)_3$, which is formed by polymerisation of ethyl isocyanate, or by distilling the cyanurate with potassium ethyl sulphate. On hydrolysis it gives

ethylamine, this confirming its constitution, which is shown by the following closed-ring formulæ to be clearly different from that of ethyl cyanurate.



Ethyl isocyanurate



Ethyl cyanurate

FULMINIC ACID, $C:NOH$, is readily volatile but unstable, and is decomposed by concentrated hydrochloric acid into hydroxylamine and formic acid, chloroformyloxime, $CHCl:N\cdot OH$, being formed as intermediate product. Kekulé regarded fulminic acid as a nitroacetonitrile, $NO_2\cdot CH_2\cdot CN$, but Nef subsequently attributed to it the constitution $C:N\cdot OH$, the carbon being divalent. With bromine, mercury fulminate (*see* p. 255) gives the compound

$$\begin{array}{l} Br\cdot C:N\cdot O \\ \quad\;\, | \qquad\; | \\ Br\cdot C:N\cdot O \end{array}$$

Silver fulminate is even more explosive than the mercury salt.

F. C. Palazzo (1907–1910) has prepared various additive products of fulminic acid with different acids (HBr, HI, $HSCN$, HNO_2, N_3H). With hydrazoic acid at $-12°$, he obtained two isomerides with different constitutions, probably with intermediate formation of Triazoformoxime:

$$N_3H + C:NOH = \begin{array}{c} H \\ N_3 \end{array}\!\!>C:N\cdot OH \longrightarrow \begin{array}{l} CH\text{——}N\text{—}OH \\ \| \qquad\quad\; | \\ N\cdot N:N \end{array}$$

Triazoformoxime · *N-hydroxytetrazole* (m pt. 145°)

The other isomeride also is possibly a tetrazole derivative.

By the action of hydrogen sulphide on mercury fulminate suspended in water, L. Cambi (1910) obtained and isolated the Formothiohydroxamic Acid predicted by Nef:

$$\begin{array}{l} H\cdot C:NO\cdot H \\ \quad\;\, | \\ H\cdot S \end{array}$$

THIOCYANIC ACID AND ITS DERIVATIVES

THIOCYANIC ACID (Rhodanic Acid), $NC\cdot SH$, is a yellow liquid of penetrating odour, stable only when anhydrous in a freezing mixture or when in very dilute aqueous solution. At ordinary temperatures it polymerises to a yellow mass. It is obtained from its mercury salt (*see later*) by the action of hydrochloric acid.

In concentrated aqueous solution, it undergoes conversion into a yellow crystalline mass of Perthiocyanic Acid, $(CN)_2S_3H_2$.

Cyanogen Sulphide, $(NC)_2S$, may be regarded as a kind of anhydride of thiocyanic acid, and is obtained from silver thiocyanate and cyanogen iodide. It forms colourless plates which have a pungent odour and are readily soluble in water.

Thiocyanuric Acid, $(NC)_3(SH)_3$, is polymeric with thiocyanic acid, and is obtained by the action of sodium sulphide on cyanogen chloride. It is a yellow powder and gives salts corresponding with a tribasic acid. Its trimethyl salt is formed by polymerisation of ethyl thiocyanate by heating at 180°.

POTASSIUM THIOCYANATE (or Rhodanate), $NC\cdot SK$, is obtained by fusing potassium cyanide with sulphur, or evaporating a solution of potassium cyanide and yellow ammonium sulphide, or, better still, by fusing potassium ferrocyanide with potassium

carbonate and sulphur; as prime material the mass used for the purification of illuminating gas is nowadays employed (vol. i, p. 651). It forms colourless prisms soluble in boiling alcohol and to a greater extent in water with absorption of heat.

AMMONIUM THIOCYANATE (or Rhodanate), $NC \cdot SNH_4$, forms colourless, tabular crystals soluble in alcohol, and readily so in water. It is obtained by heating together CS_2, NH_3, and alcohol: $CS_2 + NH_3 = NC \cdot SH + H_2S$. When heated it is transformed into the isomeric thiourea. It serves for the preparation of other thiocyanates, and is extracted in large quantities from the exhausted Laming mixture of gasworks (*see* p. 46), which contains 1 to 4 per cent. of it.

MERCURIC THIOCYANATE, $(NC \cdot S)_2Hg$, is prepared from a mercuric salt and ammonium thiocyanate, and forms a white, insoluble powder which swells up to a very considerable extent when heated (*Pharaoh's serpents*).

SILVER THIOCYANATE is precipitated as a white mass on mixing silver nitrate and ammonium thiocyanate. The latter gives, with ferric salts, a dark red coloration of FERRIC THIOCYANATE (sensitive indicator in the titration of silver with thiocyanate) and this, with potassium thiocyanate, gives a violet double salt, $(NC \cdot S)_6FeK_3$.

Hydrogen sulphide decomposes the thiocyanates, $NC \cdot SH + H_2S = NH_3 + CS_2$, while with concentrated sulphuric acid, addition of water and decomposition into ammonia and carbon oxysulphide occur

$$NC \cdot SH + H_2O = COS + NH_3.$$

For thiocyanic acid there are two series of isomeric derivatives, corresponding with the two general formulæ: $N \vdots C \cdot SX$ (alkyl thiocyanate) and $S : C : N \cdot X$ (mustard oils).

ETHYL THIOCYANATE, $NC \cdot SC_2H_5$, is a colourless liquid with a marked odour of garlic; it boils at 142° and is very slightly soluble in water. It is formed by the action of cyanogen chloride on mercaptides, or by distillation of potassium thiocyanate with potassium ethyl sulphate. As it has the constitution of a true ester, it is hydrolysed by alcoholic potash with formation of alcohol and potassium thiocyanate. But in certain reactions it behaves like the isomeric mustard oils. Nascent hydrogen converts it into merceptan, since the alkyl is united to sulphur, and the action of nitric acid in the hot yields ethylsulphonic acid.

ALLYL THIOCYANATE, $NC \cdot SC_3H_5$, boils at 161°, and has a garlic-like odour; it undergoes change into the isomeric mustard oil, slowly at the ordinary temperature and more rapidly on distillation.

The **Mustard Oils** (**Isothiocyanates**) are obtained from the corresponding thiocyanates simply by heating. They are also formed by the action of carbon disulphide on the corresponding primary amines, $CS_2 + X \cdot NH_2 = H_2S + S : C : NX$, this change taking place by way of the intermediate alkylamine salt of alkyldithiocarbamic acid (*see later*), which is distilled with mercuric chloride. Mustard oils are also formed when an alkylated thiourea is distilled with phosphoric or concentrated hydrochloric acid.

Their structure is indicated by their formation of primary amine on hydrolysis:—$S : C : NX + 2H_2O = CO_2 + H_2S + X \cdot NH_2$. The isothiocyanic acid, $S : C : NH$, from which these mustard oils are regarded as derived, is not known in the free state.

METHYL MUSTARD OIL (Methyl Isothiocyanate), $SC : NCH_3$, melting at 34° and boiling at 119°; Ethyl Mustard Oil, $SC : NC_2H_5$, boiling at 134°; and Propyl Mustard Oil, $SC : NC_3H_7$, boiling at 153°, are of little importance. More interesting is

ALLYL MUSTARD OIL (or Ordinary Mustard Oil; Allyl Isothiocyanate), $S : C : NC_3H_5$, which is prepared by distilling *Sinapis nigra* (*black mustard*) with water; it is obtained synthetically by the reactions given above. It is a liquid with a pungent odour recalling that of mustard and raises blisters on the skin; it is sparingly soluble in water and boils at 150·7°.

CYANAMIDE AND ITS DERIVATIVES

CYANAMIDE, $NC\cdot NH_2$, is a white crystalline substance, melting at 40° and dissolving very slightly in water, alcohol, or ether. It is obtained by passing a current of cyanogen chloride into an ethereal solution of ammonia: $2NH_3 + NC\cdot Cl = NH_4Cl + NC\cdot NH_2$. It is also formed by desulphurising thiourea, $NH_2\cdot CS\cdot NH_2$, by means of HgO, which removes H_2S.

It is obtained abundantly and in a pure state by extracting calcium cyanamide (*see later*) systematically with water, neutralising the saturated solution with sulphuric acid, filtering from the calcium sulphate, concentrating in a vacuum, again filtering from the gypsum, concentrating anew, and extracting the crystalline mass—formed on cooling—with ether, which does not dissolve gypsum, dicyanamide, and other impurities. Evaporation of the ether yields pure cyanamide in almost theoretical yield (Baum, 1910).

With lapse of time, or rapidly at 150°, cyanamide changes into the polymeric dicyanodiamide (*see later*). It behaves both as a weak base forming unstable crystalline salts, and as a weak acid giving metallic salts, *e.g.* $NC\cdot NHNa$, $NC\cdot NAg_2$, &c. The most important of these is **calcium cyanamide**, $NC\cdot NCa$, which was considered in detail in vol. i, p. 309, in the discussion of the utilisation of atmospheric nitrogen; it is formed by the action of nitrogen on calcium carbide and forms an excellent nitrogenous fertiliser.

In presence of dilute acid, cyanamide fixes a molecule of water, giving urea: $NC\cdot NH_2 + H_2O = NH_2\cdot CO\cdot NH_2$; with hydrogen sulphide it yields thiourea. Cyanamide also gives two series of isomeric alkyl derivatives of the general formulæ $N:C\cdot NX_2$ and $XN:C:NX$. Compounds of the latter formula are derived from the hypothetical *carbodi-imide*, $NH:C:NH$; for example, *carbodiphenylimide*, $C_6H_5N:C:NC_6H_5$, boiling at 330°, is well characterised.

DIETHYLCYANAMIDE, $NC\cdot N(C_2H_5)_2$, is formed by the action of ethyl iodide on the silver salt of cyanamide, its structure being indicated by the products—$CO_2 + NH_3 + NH(C_2H_5)_2$—obtained on hydrolysis with dilute acid. *Methyl-* and *ethyl-cyanamide* are also known.

DICYANODIAMIDE, $(NC\cdot NH_2)_2$, is formed, as has already been mentioned, from cyanamide; certain of its reactions indicate the structure $NC\cdot NH\cdot C\begin{matrix}\diagup NH \\ \diagdown NH_2\end{matrix}$ (Bamberger). It forms acicular crystals or small flat prisms. When heated strongly and rapidly, it is converted into a white insoluble powder, MELAM, $C_6H_9N_{11}$ or $[(NC)_3(NH_2)_2]_2NH$, this being an imide of melamine, into which it is transformed by sulphuric acid or ammonia.

MELAMINE (Cyanurtriamide), $(NC)_3(NH_2)_3$, is a crystalline basic substance, insoluble in alcohol or ether. When it is boiled with acid, the amino-groups are gradually replaced by hydroxyl groups, giving AMMELINE, $(NC)_3(NH_2)_2OH$, then AMMELIDE, $(NC)_3NH_2(OH)_2$, and finally **Cyanuric Acid**, $(NC)_3(OH)_3$.

As usual, the alkyl derivatives form two isomeric series, derivatives being known of a hypothetical **Isomelamine**, $(CNH)_3(NH)_3$, among these being the polymerised alkylcyanamides.

VII. DERIVATIVES OF CARBONIC ACID

True carbonic acid, $O:C(OH)_2$, is not known in the free state, since two hydroxyl groups cannot exist in combination with the same carbon atom (*see* p. 182), but it is supposed to exist in aqueous solution, and salts corresponding with this formula are stable and well known (carbonates and bicarbonates). Also important organic derivatives, similar to those already studied for other dibasic acids (amides, chlorides, esters, &c.), are known. The acid derivatives are less stable than the normal ones.

ESTERS OF CARBONIC ACID

ETHYL CARBONATE, $CO(OC_2H_5)_2$, is a liquid which is insoluble in water, boils at 126°, and has a pleasant odour. It is formed by the interaction of ethyl chlorocarbonate and alcohol: $C_2H_5 \cdot OH + Cl \cdot CO \cdot OC_2H_5 = HCl + CO(OC_2H_5)_2$, and also from silver carbonate and ethyl iodide. Mixed esters, containing different alkyls, also exist.

ETHYLCARBONIC ACID, $CO(OH) \cdot OC_2H_5$, is known only as salts, *e.g.* **Potassium Ethylcarbonate**, $CO(OK) \cdot OC_2H_5$, which is obtained by the action of CO_2 on an alcoholic solution of potassium ethoxide and forms shining scales, giving alcohol and potassium carbonate when treated with water.

CHLORIDES OF CARBONIC ACID

Carbon Oxychloride (*phosgene*), $COCl_2$, has already been described (vol. i, p. 394).

CHLOROCARBONIC ACID, $COCl \cdot OH$, is the acid chloride of carbonic acid, but is not stable and, when liberated, decomposes into CO_2 and HCl. Its esters are, however, well known, the action of phosgene on absolute alcohol giving, for example, ethyl chlorocarbonate (**Ethyl Chloroformate**), $Cl \cdot CO \cdot OC_2H_5$, thus: $C_2H_5 \cdot OH + COCl_2 = HCl + Cl \cdot CO \cdot OC_2H_5$.

This ester is a liquid, having a pungent odour, boiling at 93° and readily decomposing under the action of water; it is used largely in organic syntheses to introduce carboxyl into the molecule.

AMIDES OF CARBONIC ACID

The acid amide, $NH_2 \cdot CO \cdot OH$, is **Carbamic Acid**, and the normal amide, $NH_2 \cdot CO \cdot NH_2$, *urea*.

CARBAMIC or **CARBAMINIC ACID**, $NH_2 \cdot CO \cdot OH$, is obtained as ammonium salt —*ammonium carbamate*, $NH_2 \cdot CO \cdot ONH_4$—by the direct union of dry CO_2 and NH_3; a white mass is thus obtained which, even at 60°, dissociates into $CO_2 + NH_3$. In aqueous solution this salt does not precipitate solutions of calcium salts at the ordinary temperature, since calcium carbamate is soluble, but in the hot the salt decomposes into CO_2 and NH_3 and gives a precipitate of calcium carbonate.

Ethyl carbamate or **URETHANE**, $NH_2 \cdot CO \cdot OC_2H_5$, is also well known and is obtained by the action of ammonia or ethyl carbonate, $CO(OC_2H_5)_2 + NH_3 = C_2H_5 \cdot OH + NH_2 \cdot CO \cdot OC_2H_5$, or, more easily, by treating ethyl chlorocarbonate with ammonia:

$$COCl(OC_2H_5) + 2NH_3 = NH_4Cl + NH_2 \cdot CO \cdot OC_2H_5.$$

It melts at 48° to 50°, is soluble in water, and is used as a *soporific*.

The following are also known: *iodourethane*, $NHI \cdot CO \cdot OC_2H_5$; *ethylurethane*, $NHC_2H_5 \cdot CO \cdot OC_2H_5$ (boils at 175°); *nitrourethane*, $NO_2 \cdot NH \cdot CO \cdot OC_2H_5$; *carbamidyl chloride*, $NH_2 \cdot CO \cdot Cl$ (melts at 50° and boils at 61°); and *diethyl iminodicarbonate*, $NH(CO \cdot OC_2H_5)_2$, which is the imide of urethane.

Urethane derivatives are readily hydrolysable with alkalis and yield ammonia and urea when heated.

UREA (Carbamide), $CO(NH_2)_2$, is the final oxidation product of nitrogenous compounds in the living organism, and the adult human being produces about 30 grms. of it a day; it is found in general in the urine of carnivora (where it was first discovered) and in other animal fluids. It crystallises in shining needles soluble in water and in alcohol, but insoluble in ether; it melts at 132° and sublimes in a vacuum. It is formed from ammonium cyanate by simple rearrangement under the action of heat (Wöhler): $NC \cdot ONH_4 = CO(NH_2)_2$. Escales (1911) found that when urea is distilled or sublimed in a vacuum, the reverse reaction, *i.e.* formation of ammonium cyanate, occurs. Urea is also obtained by the action of ammonia on ethyl carbonate or carbamic acid:

$$CO(OC_2H_5)_2 + 2NH_3 = 2C_2H_5 \cdot OH + CO(NH_2)_2.$$

Many other reactions give urea, *e.g.* oxidation of thiourea, action of water on cyanamide, &c., but in the laboratory it is prepared by treating with barium carbonate the urea nitrate obtained by evaporating urine in presence of nitric acid, or by heating ammonium sulphate solution with potassium ferrocyanide or cyanate:

$$(NH_4)_2SO_4 + 2NCOK = K_2SO_4 + 2CO(NH_2)_2.$$

When heated it is decomposed into ammonia, biuret (*see later*), cyanuric acid, and ammelide. It is readily hydrolysed by acids, alkalis, or even hot water: $CO(NH_2)_2 + H_2O = CO_2 + 2NH_3$, and is decomposed by nitrous acid or sodium hypochlorite:

$$2HNO_2 + CO(NH_2)_2 = 3H_2O + CO_2 + 2N_2.$$

It exhibits the properties of a base and of a weak acid, giving salts with acids (*e g.* **Urea Nitrate,** $CO(NH_2)_2, HNO_3$, which is soluble in water and slightly so in nitric acid, and with concentrated sulphuric acid gives the highly acid **Nitrourea,** $NH_2\cdot CO\cdot NH\cdot NO_2$), and with bases, *e.g.* $CO(NH_2)_2, 2HgO$. It also crystallises with other salts, *e.g.* $CO(NH_2)_2 + NaCl + H_2O$, $CO(NH_2)_2 + AgNO_3$, &c. Mercuric nitrate precipitates urea quantitatively from its neutral aqueous solutions as $2CO(NH_2)_2 + Hg(NO_3)_2 + 3HgO$.

Urea forms various *alkyl derivatives*; thus ethyl cyanate and ethylamine give *symm.* or *α-diethylurea*, which is isomeric with *unsymm.* or *β*-diethylurea, $NH_2\cdot CO\cdot N(C_2H_5)_2$: $CO\cdot NC_2H_5 + C_2H_5\cdot NH_2 = CO(NHC_2H_5)_2$. The constitutions of these alkyl derivatives are determined by study of the products of their hydrolysis.

Readily hydrolysable *alkylisoureas*, $NH : C\mathord{<}^{NH_2}_{OX}$, are also known.

SEMICARBAZIDE, $NH_2\cdot CO\cdot NH\cdot NH_2$, which is obtained from potassium cyanate and hydrazine hydrate, may also be regarded as a derivative of urea. It has already been seen that this base (which melts at 96°) gives crystalline compounds (*semicarbazones*) with ketones and aldehydes (*see* p. 206). **CARBAZIDE** (Carbohydrazide), $CO(NH\cdot NH_2)_2$, melts at 152°, and is obtained from esters of carbonic acid by the action of hydrazine hydrate.

Acetylurea, $NH_2\cdot CO\cdot NH\ CO\cdot CH_3$, and **Allophanic Acid,** $NH_2\cdot CO\cdot NH\cdot CO_2H$ (not known free, but as salts), are obtained from acid chlorides and urea.

The formation of *ureides* (compounds of urea and mono- and dibasic acids) takes place with monobasic divalent acids or with an alcohol and acid. Such a reaction gives **Hydantoic Acid** (*glycoluric acid*), $NH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, which, when evaporated in presence of HCl, loses water and forms **Hydantoin,** $CO\mathord{<}\begin{matrix} NH\cdot CO \\ | \\ NH\cdot CH_2 \end{matrix}$, the latter giving first hydantoic acid and then CO_2, NH_3, and glycine on hydrolysis.

When urea is heated at 160°, 2 mols. condense with separation of ammonia and formation of **Biuret,** $NH\mathord{<}\begin{matrix} CO\cdot NH_2 \\ | \\ CO\cdot NH_2 \end{matrix}$, which crystallises with $1H_2O$ and is soluble in water or alcohol; in alkaline solution it gives a characteristic violet coloration with a little copper sulphate.

DERIVATIVES OF THIOCARBONIC ACID

More or less complete substitution of the oxygen of carbonic acid by sulphur gives a series of unstable compounds, which form stable alkyl derivatives and exhibit various cases of isomerism indicated by varying products of hydrolysis. These numerous sulphur compounds are reducible to three types, according as they contain (1) the nucleus $SC\mathord{<}$, *thiocarbonic* or *thiocarbamic compounds*, (2) the nucleus $OC\mathord{<}$, *carbonyl* or *carbamic compounds*, or (3) the group $H\cdot N : C\mathord{<}$, *iminocarbonic* or *iminocarbamic compounds*.

The following are the principal compounds of these types, which have been thoroughly studied in the form of their alkyl derivatives:

Trithiocarbonic acid . .	$SC(SH)_2$	Monothiocarbamic acid .	$SC\mathord{<}^{NH_2}_{OH}$
Dithiocarbonic acid . .	$SC\mathord{<}^{SH}_{OH}$	Thiocarbamide . . .	$SC\mathord{<}^{NH_2}_{NH_2}$
Monothiocarbonic acid . .	$SC\mathord{<}^{OH}_{OH}$	Thiophosgene	$SC : Cl_2$
Dithiocarbamic acid . .	$SC\mathord{<}^{NH_2}_{SH}$	Thiocarbamidyl chloride .	$SC\mathord{<}^{NH_2}_{Cl}$

Dithiocarbonylic acid . .	$CO(SH)_2$	Iminodithiocarbonic acid	$HN : C(SH)_2$
Monothiocarbonylic acid . .	$CO<^{SH_2}_{OH}$	Iminomonothiocarbonic acid	$HN:C<^{SH}_{OH}$
Monothiocarbonylamic acid .	$CO<^{NH_2}_{SH}$	Iminothiocarbamic acid .	$HN : C<^{NH_2}_{SH}$

THIOPHOSGENE (**Carbon Sulphochloride**), $SCCl_2$, is a red liquid which fumes in the air, attacks the mucous membrane, and boils at 68° to 74°. It is prepared by the action of chlorine on carbon disulphide, the intermediate compound, $CCl_3\cdot SCl$, thus obtained being reduced with stannous chloride. It is more stable towards water than phosgene, and with ammonia gives, not thiourea, but ammonium thiocyanate.

TRITHIOCARBONIC ACID, CS_3H_2, is obtained as sodium salt by the action of carbon disulphide on sodium sulphide. The free acid is a brown unstable oil and its *ethyl ester*, $SC(SC_2H_5)_2$, a liquid boiling at 240°.

POTASSIUM XANTHATE, $KS\cdot SC\cdot OC_2H_5$, is the ether of the potassium salt of dithiocarbonic acid. It is formed by the action of CS_2 on $C_2H_5\cdot OK$ and crystallises in shining needles soluble in water and to a less extent in alcohol. With copper sulphate it gives copper xanthate as an unstable yellow powder which is used in indigo printing.

XANTHIC or **XANTHONIC ACID**, $HS\cdot SC\cdot OC_2H_5$, is liberated from its potassium salt (*see above*) and forms an oil insoluble in water; it readily decomposes into $C_2H_5\cdot OH + CS_2$.

DITHIOCARBAMIC ACID, $NH_2\cdot SC\cdot SH$, is obtained as ammonium salt by the action of ammonia on an alcoholic solution of CS_2:

$$2NH_3 + CS_2 = NH_2\cdot SC\cdot SNH_4.$$

In the free state this acid forms an unstable, reddish oil (decomposing into SH_2 + thiocyanic acid) and its ethyl ester, $NH_2\cdot SC\cdot SC_2H_5$, is *dithiourethane*, whilst *thiourethane* will be $NH_2\cdot CO\cdot SC_2H_5$ and is isomeric with *xanthogenamide*, $NH_2\cdot CS\cdot OC_2H_5$.

Ethylamine Ethyldithiocarbamate, $C_2H_5\cdot NH\cdot SC\cdot SH, NH_2\cdot C_2H_5$, is formed similarly by the action of carbon disulphide on ethylamine; in the hot it gives *diethylthiourea*, $SC(NHC_2H_5)_2$, the mercuric salt of which gives the corresponding mustard oil with water in the hot, whilst the alkylated dithiocarbamic acids obtained with secondary amines do not give mustard oils under these conditions.

THIOCARBAMIDE (**Thiourea**), $SC(NH_2)_2$, is only partly obtained on heating ammonium thiocyanate at 130°, the reaction being reversible. It forms crystals melting at 172°, and dissolving in water and in alcohol, giving neutral solutions; it has a bitter taste. On hydrolysis it yields $CO_2 + H_2S + NH_3$. As has already been stated, it is converted into urea by permanganate, cyanamide by mercuric oxide, and potassium thiocyanate and ammonia by alcoholic potash at 100°. It behaves as a weak acid and a weak base, and its derivatives, in some cases, correspond with the tautomeric formula, $HNC<^{NH_2}_{SH}$ (hypothetical *iminothiocarbamic acid*).

About 10,000 kilos of thiourea are produced annually by two factories, one French and the other German, for preserving loaded silk from corrosion, the Gianoli process (*see later*, under Silk) being used. Owing to this, the price of thiourea has been lowered from £2 to 5*s*. 6*d*. or 6*s*. 6*d*. per kilo.

Acetylthiourea, Sulphohydantoin, &c. are also known.

GUANIDINE AND ITS DERIVATIVES

GUANIDINE (**Iminourea** or **Iminocarbamide**), $NH : C<^{NH_2}_{NH_2}$ forms crystals readily soluble in water or alcohol. It is a strong base, absorbing carbon dioxide from the air, but is converted into salts by one equivalent of acid. The fatty acid salts are converted on heating into *guanamines*, which form crystals of peculiar shape.

It is obtained by heating cyanamide with ammonium iodide:

$NH_4I + CN\cdot NH_2 = NH : C(NH_2)_2 . HI$; or, better, as thiocyanate by heating thiourea with ammonium thiocyanate at 190°:

$$NCS\cdot NH_4 + SC(NH_2)_2 = H_2S + NH : C(NH_2)_2, NC\cdot SH.$$

It may also be obtained from dicyanodiamide by the action of aqua regia (C. Ulpiani, 1907).

Guanidine is readily hydrolysed, forming first ammonia and urea and then CO_2 and NH_3.

Guanidine Nitrate, $NH : C(NH_2)_2, HNO_3$, is converted by concentrated sulphuric acid into *nitroguanidine*, $NH : C(NH_2)(NH\cdot NO_2)$, and this, on reduction, gives *aminoguanidine*, $NH : C(NH_2)(NH\cdot NH_2)$. The latter gives hydrazine, $(NH_2)_2$, NH_3, and CO_2 on hydrolysis with acid or alkali, whilst with nitrous acid it yields **Diazoguanidine** (*iminocarbamidazide*), $NH : C(NH_2)\cdot N_3$, which is resolved by alkali into hydrazoic acid (*see* vol. i, p. 327) and cyanamide.

From aminoguanidine can be obtained **Azodicarbonamide**, $NH_2\cdot CO\cdot N : N\cdot CO\cdot NH_2$, and **Hydrazodicarbonamide**, $NH_2\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH_2$.

GLYCOCYAMINE, $NH : C(NH_2)\cdot NH\cdot CH_2\cdot CO_2H$, is formed by the union of glycocoll with cyanamide, and if water is lost **Glycocyamidine**, $NH : C<\begin{array}{l}NH\cdot CO\\ \quad\;\; |\\ NH\cdot CH_2\end{array}$, is obtained. If however, instead of glycocoll, its methyl-derivative is taken, *sarcosine*, $CO_2H\cdot CH_2\cdot NH\cdot CH_3$ (melts at 115° and is neutral), results, *creatine* and *creatinine* being obtained similarly.

CREATINE, $NH : C(NH_2)\cdot N(CH_3)\cdot CH_2\cdot CO_2H$, is obtained from meat-extract, being a stable component of muscle. It has a neutral reaction and is soluble in water and sparingly so in alcohol; it crystallises with $1H_2O$, has a bitter taste and, when heated with acid, loses 1 mol. of water of constitution and forms creatinine; on complete hydrolysis, it gives urea and sarcosine.

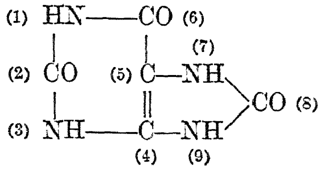
CREATININE, $NH : C<\begin{array}{l}NH\text{——}CO\\ \qquad\quad\;\; |\\ N(CH_3)\cdot CH_2\end{array}$ is a weak base and dissolves very readily in water, giving creatine again. It is one of the constituents of urine and forms a characteristic zinc salt, 2 mols. of creatinine combining with 1 mol. of $ZnCl_2$. When hydrolysed, it gives ammonia and methylhydantoin.

URIC ACID AND ITS DERIVATIVES

When the two amino-groups of urea condense with the two carboxyl groups of a dibasic acid with expulsion of 2 mols. of water, *ureides* (*see above*) are obtained. Thus oxalic acid yields *parabanic acid*, $CO<\begin{array}{l}NH\cdot CO\\ \qquad\;\; |\\ NH\cdot CO\end{array}$; malonic acid, *barbituric acid*, $CO<{NH\cdot CO \atop NH\cdot CO}>CH_2$; tartronic acid, *dialluric acid*, and mesoxalic acid, *alloxan*, $CO<{NH\cdot CO \atop NH\cdot CO}>CO$. If, however, only one molecule of water is eliminated, one amino- and one carboxyl-group remaining unchanged, *uroacids* are obtained, *e.g. oxaluric acid*, $NH_2\cdot CO\cdot NH\cdot CO\cdot CO_2H$, and *alloxanic acid* (from mesoxalic acid).

These ureides are usually well crystallised, and are aminic and also markedly acid in character. On hydrolysis, they give first the corresponding uroacid and then urea and free acid. They are sometimes formed on oxidation of diureides (*see below*); thus *parabanic acid* is obtained by oxidising uric acid with nitric acid. The alcohol-acids and the aldehydo-acids also give such condensations (*see above*), yielding, for example, *hydantoin*, *hydantoic acid*, and *allanturic acid* (from glyoxylic acid).

When 2 mols. of urea take part in the condensation, *diureides* are obtained, these forming the uric acid group :

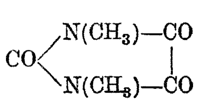


and its derivatives : *xanthine, caffeine, theobromine, guanine, hypoxanthine, alloxanthine, purpuric acid, allantoin*, &c. The positions of the substituent groups are indicated by the bracketed numbers shown in the above formula for uric acid. During recent years successful attempts have been made, by means of ethyl cyanoacetate, to synthesise all these xanthine bases and to convert them, one into the other (see *Berichte der deutsch. chem. Gesells.*, 1899, 32, p. 435).

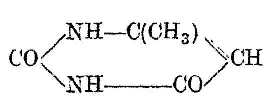
As a general rule, the ureides and diureides have a more or less marked acid character and, as they contain no carboxyl group, this acidity is explained as due to the existence of these compounds in tautomeric forms, just as is the case with *succinimide*, $\begin{matrix} CH_2-CO \\ | \\ CH_2-CO \end{matrix} \!\!> NH$. In the latter, it is assumed that the iminic hydrogen atom is very mobile and undergoes displacement and union with the oxygen of the neighbouring carbonyl group, a double linking between carbon and nitrogen being formed and an acid hydroxyl group capable of forming salts with metals. The tautomeric formula of Succinimide would hence be $\begin{matrix} CH_2\cdot C(OH) \\ | \\ CH_2-\!\!-CO \end{matrix} \!\!> N$, and that of Parabanic Acid $CO <\!\! \begin{matrix} N : C\cdot OH \\ | \\ N : C\cdot OH \end{matrix}$; similar formulæ hold for *uric acid* and barbituric acid, the latter functioning as a dibasic acid (in this case, however, the acid character is perhaps to be attributed to the hydrogen of the methylene group, CH_2).

Several diureides are found in nature, *e.g.* in guano, in the urine and muscles of carnivora, in the excreta of serpents, in articular concretions, and in certain plants (theobromine in cocoa, caffeine, &c).

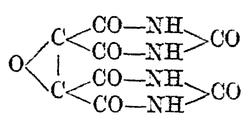
The constitutional formulæ of the more important diureides are as follow :



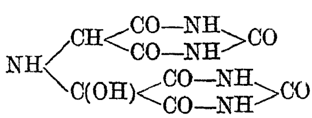
Dimethylparabanic acid (cholestrophane)



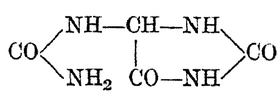
Methyluracyl



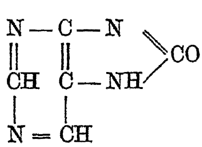
Alloxanthine



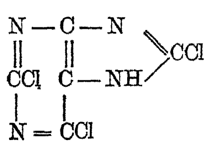
Murexide



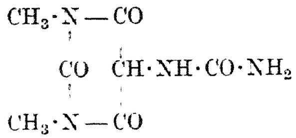
Allantoin



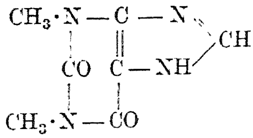
Purine



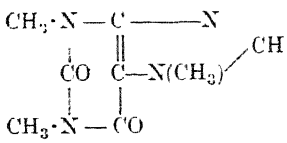
Trichloropurine



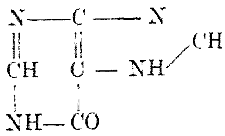
Dimethylpseudouric acid



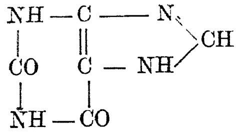
Theophylline



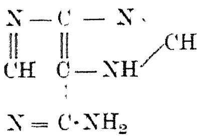
Caffeine



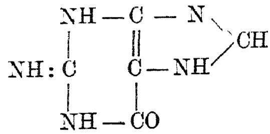
Hypoxanthine



Xanthine

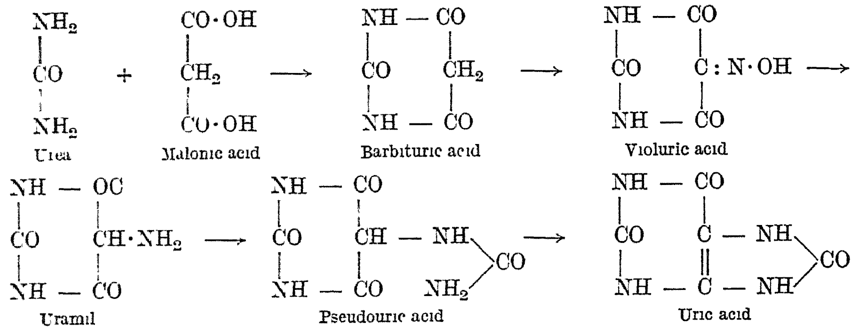


Adenine



Guanine

URIC ACID, $C_5H_4O_3N_4$. Syntheses of uric acid are many and various; from cyanoacetic acid, or glycocoll or isodialuric acid, by heating with urea; from aminobarbituric acid and potassium cyanate; from ethyl acetoacetate and urea, passing through methyluracyl, nitrouracyl, hydroxyuracyl, and isodialuric acid. The following scheme represents the various steps of the synthesis from malonic acid:[1]

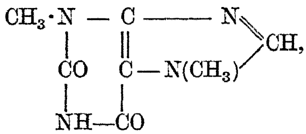


Urea — Malonic acid — Barbituric acid — Violuric acid — Uramil — Pseudouric acid — Uric acid

Uric acid is a feeble dibasic acid (*see above*), and forms a white, amorphous substance insoluble in alcohol or ether and almost insoluble in water. It dissolves, however, in concentrated sulphuric acid, from which it separates unchanged on dilution with water. It is extracted from guano, the excrements of serpents, and the urine of carnivora.

Evaporation of uric acid with dilute nitric acid and treatment of the residue with ammonia yields *murexide*, which forms yellowish green crystals which give a purple aqueous solution, turning blue on addition of alkali (characteristic reaction for uric acid).

THEOBROMINE (3 : 7-Dimethyl-2 : 6-dioxypurine), $C_7H_8O_2N_4$ or



is extracted from *cocoa*,[2] and forms white, bitter-tasting crystals, slightly soluble in water

[1] The *constitution of uric acid* was demonstrated first by Medicus, and later, by various syntheses, by E Fischer (Liebig's *Annalen*, 1882, 215, p. 253). The presence of a chain, —C—C—C—, and of a carbonic acid residue is shown by the formation of urea and alloxan when uric acid is treated in the cold with nitric acid. The presence of four imino-groups is deduced from the fact that, by introduction of four methyl groups and subsequent hydrolysis, the four atoms of nitrogen are eliminated as methylamine. A large part of the uric acid molecule is rendered evident by the formation of allantoin (of known constitution) on oxidation with alkaline permanganate, and by the formation of methylurea and methylalloxan on oxidation of dimethyluric acid.

[2] **Cocoa and Chocolate.** Cocoa is placed on the market in the form of large violet seeds of *Theobroma cacao*, which grows well in the Antilles, Mexico, Guatemala, Java, Borneo, Esmerelda (equator), &c. The red or brown

or alcohol. It behaves as a weak acid and a weak base. With methyl iodide, the silver salt yields *caffeine*.

CAFFEINE,[1] $C_8H_{10}O_2N_4 + H_2O$ (constitution given above), is identical with theine[2]; it forms shining needles which readily sublime, are sparingly soluble in alcohol and in water, and have a rather bitter taste. Synthetically it is obtained, for example, from ethyl cyanoacetate or malonic acid and dimethylurea.

GUANINE, $C_5H_5ON_5$ (constitution given above), is a di-acid base, but forms salts also with bases. It is a white powder insoluble in water but soluble in ammonia. On oxidation with potassium chlorate and hydrochloric acid, it gives carbon dioxide, parabanic acid, and guanidine.

XANTHINE, $C_5H_4O_2N_4$ (constitution given above), is a white powder and acts as both acid and base. It is obtained from guanine by the action of nitrous acid, and its lead salt reacts with methyl iodide, giving theobromine.

ADENINE, $C_5H_5N_5$ (constitution given above), forms shining needles and is a base occurring in tea and in ox-pancreas. It is formed by decomposition of the nuclein of the cell-nuclei and is hence of physiological importance.

VIII. ESTERS

(Oils, Fats, Waxes, Candles, Soaps)

The compounds or *esters* formed by alcohols with inorganic acids have already been studied (*see* p. 196), and we shall now consider the esters resulting

mature fruits resemble cucumbers, each containing 50 to 60 seeds like beans. The seeds are separated from the pulp, heaped in casks for 4 to 5 days to initiate the fermentation which increases the perfume, and then dried in the sun The chemical composition differs considerably with the variety: fatty substance (*cocoa-butter*), 35 to 45 per cent.; proteins, 3 to 18 per cent.; cellulose, 3 to 25 per cent.; gums and starch, 3 to 15 per cent.; ash, 3 to 4 per cent. *Cocoa-butter* (or cacao-butter) is extracted by pressing the seeds hot, and forms a faintly yellow mass of pleasing odour; it melts at 29° to 31°, and contains the glycerides of arachic, palmitic, oleic, stearic, and lauric acids.

In the manufacture of chocolate, the seeds are washed in suitable sieves and then gently and cautiously heated for 30 to 40 minutes to facilitate skinning They are next crushed in mortars or rotating cylinders, the flour obtained being made into a paste with sugar and is worked for a long time on stone rollers, different ingredients and flavouring matters being added to give the different kinds of chocolate; the homogeneous paste then passes to the moulds Good chocolate contains from 40 to 60 per cent of cocoa, the rest being sugar; ordinary qualities contain 10 to 15 per cent of starch.

Italy imported 12,000 quintals of cocoa in 1901, 93,000 in 1908, and 24,000 (including 5200 quintals in powder or paste), worth £185,200, in 1910, in addition to 3380 quintals of cocoa-butter of the value of £48,680. Cocoa costs about £8 per quintal, and pays an import duty of £4 (in Italy). The imports of chocolate into Italy were 8000 quintals in 1901; 10,900 in 1908; 15,000, worth £180,000, in 1910; the import duty being £5 4*s*. per quintal. Italy exports, on the average, 2300 quintals of chocolate, of the value £28,000, per annum.

[1] Coffee consists of the seeds of one of the Rubiaceæ (*Coffea arabica*), which grows spontaneously in Southern Ethiopia and Arabia, and is cultivated on an enormous scale in India, the Antilles, Madagascar, and South America. It is an evergreen plant, 6 to 9 metres high and of pyramidal habit, with greyish branches and lanceolated leaves, the flowers (at the base of the leaf) being white and pleasant-smelling, like jessamine. The fruit forms drupes like cherries, the epicarp passing from yellow to green to red to brownish, and the mesocarp being yellow and of agreeable taste The endocarp is divided into two compartments surrounded by coriaceous membrane and each containing a seed, which has one convex and one flat, furrowed face, and is covered by a friable pellicle the endosperm (albumen) is yellowish or greenish and horny.

The form of the seed varies with the kind of the coffee (*Coffea mauritiana, laurina, liberica, &c.*). Mocha coffee berries are small and the Australian ones large, whilst those from the Antilles are intermediate in size.

The cultivation of coffee has received a considerable impulse in Brazil, where as much as 400,000 tons (almost half the total production of the world) are now produced. Of the Antilles coffees, the most highly valued is that from Porto Rico.

Coffee berries are composed of celluloses (18 per cent.), fatty matters (12 per cent), gummy and saccharine substances (10 per cent), nitrogenous compounds (12 per cent.), mineral salts (4 to 5 per cent.), a tannin (*caffetannic acid*, 8 per cent.), caffeine (0 8 to 1 3 per cent), *caffearine* and water (11 per cent.). When roasted, coffee develops aroma and loses 15 to 20 per cent. in weight, but increases in volume by one-third, while the sugar caramelises and the cellulose carbonises partially, forming a brown oil which is denser than water, dissolves in ether, and constitutes the aromatic substance (*caffeone*) *Roasted coffee* contains, on the average, 1·5 per cent. of water, 13 per cent. of nitrogenous substances, 0 8 per cent. of sugars, 13 5 per cent. of fats, 4·8 per cent. of ash, 0 9 per cent. of caffeine, and 46 per cent. of non-nitrogenous substances; to hot water this coffee gives up about 25 per cent. of its weight.

In 1900 Italy imported 141,000 quintals of coffee; in 1908, 227,600 quintals; and in 1910, 253,000 quintals (about four-fifths from Brazil), of the value of £1,062,080; the former Customs duty of £6 per quintal was lowered slightly in 1909.

[2] Tea is an evergreen shrub, *Thea chinensis* (order Ternstrœmiaceæ), cultivated in China, Japan, British India, Java, Ceylon, and Brazil. The leaves (similar to those of the white willow) are twisted, dried, and folded, prior to rapid immersion in boiling water and drying on heated plates (4 kilos of leaves yield 1 kilo of tea). Commercially the numerous varieties are grouped into three types: green, black, and scented, the last two being slightly fermented. The active alkaloid is Theine (*see above*). The best infusion of tea is obtained by macerating for thirty minutes in cold water and then adding boiling water, the liquid being poured off before it becomes very brown and excessively rich in tannin (20 grms. of tea per litre of slightly hard water). France imported 475,000 kilos of tea in 1882 and 1,160,000 kilos in 1906. Italy imported 69,000 kilos in 1908 and 73,600 kilos, of the value of £11,120, in 1910, the Customs duty being £10 per quintal.

from the substitution of the typical hydrogen of organic acids by alkyl radicals. Various isomerides exist with these compounds, *e.g.* methyl butyrate is isomeric with ethyl propionate, butyl formate with propyl acetate. Attention will, however, more especially be paid to the esters of glycerine (*glycerides*), since on these are based the fat, oil, soap, and candle industries.

PREPARATION. These esters can be obtained by the general methods already described (*loc. cit.*), *e.g.* by the action of the acid chlorides or anhydrides on the alcohols or sodium alkoxides:

$$C_2H_5 \cdot CO \cdot Cl + C_2H_5 \cdot OH = HCl + C_2H_5 \cdot COOC_2H_5.$$

They are also formed by the interaction of the silver salt of the acid and the alkyl iodide, and by the action of gaseous hydrogen chloride on a hot alcoholic solution of the nitrile of the acid. Further, the alcohols and acids themselves react, slowly in the cold and more rapidly although not completely in the hot, with formation of esters:

$$C_2H_5 \cdot OH + CH_3 \cdot CO_2H = CH_3 \cdot CO_2C_2H_5 + H_2O.$$

In practice the preparation is carried out as follows: the dry organic acid is mixed with an excess of absolute alcohol and the mixture saturated with dry hydrogen chloride gas, left for some time in a moderately warm place and then poured into water; the ester separates in an insoluble form after neutralisation of the aqueous liquid with alkali in the cold.

In this reaction the acid chloride is probably formed as an intermediate product: $CH_3 \cdot CO_2H + HCl = H_2O + CH_3 \cdot CO \cdot Cl$; the latter—which with water might give the reverse reaction—being in presence of excess of the alcohol, forms the ester (equation given above). But esterification is never complete, the reaction being a reversible one:

$$C_nH_{2n+1} \cdot OH + C_nH_{2n}O_2 \rightleftharpoons H_2O + C_nH_{2n-1}O_2 \cdot C_nH_{2n+1}.$$

After a certain time a system is obtained which contains given quantities of alcohol (a), acid (b), water and ester (z). The same equilibrium is attained by mixing 1 mol. of ester and 1 mol. of water as by mixing 1 mol. of acid and 1 mol. of alcohol, and this equilibrium is represented by the following equation for bimolecular reactions (*see* vol. i, p. 67): $k(a-z)(b-z) = k_1z^2$, where a and b represent the respective initial concentrations of alcohol and ester and z that of the ester and water when equilibrium is reached, all expressed in *mols.* (gram-molecules); k and k_1 are constants depending on the nature of the reaction and, according to a definite law, slightly on the temperature. If, for convenience, $\frac{k_1}{k}$ is made equal to K, the equation becomes: $(a-z)(b-z) = Kz^2$.

With 46 grms. of alcohol and 60 grms. of acetic acid (gram-molecules), it is found experimentally that $K = 0{\cdot}25$, and, as a and b both assume the value 1, 1 mol. of each reacting, the equation becomes $(1-z)^2 = 0{\cdot}25\,z^2$, *i.e.* $1-z = 0{\cdot}5\,z$ or $z = \frac{2}{3}$. This means that when a state of equilibrium is reached, the system contains $\frac{1}{3}$ mol. of acetic acid + $\frac{1}{3}$ mol. of alcohol + $\frac{2}{3}$ mol. of ester + $\frac{2}{3}$ mol. of water. Every substance participating in the equilibrium acts in proportion to its mass. If the above equation is given the form $\frac{a-z}{z} = K\frac{z}{b-z}$, it becomes evident that, in order to displace the equilibrium so as to have a greater value of z (*i.e.* of esterification), the value of a must be increased and that of b decreased, esterification being complete when $a = \infty$. The same final result is obtained when b is much greater than a, esterification again being complete when $b = \infty$. In practice, almost complete esterification is attained when 1 mol. of acid is employed per 10 mols. of alcohol or *vice versa*. That the same result is obtained with excess of alcohol as with excess of acid is shown by the above equation, since, if instead of m mols. of both acid and alcohol, n times as many molecules of acid are taken, the equation becomes: $\frac{m-z}{z} = K\frac{z}{n.m-z}$; whilst if n times as many molecules of alcohol are

taken, it becomes: $\frac{n.m - z}{z} = K \frac{z}{m - z}$. But these two equations are identical, multiplication of the terms of the former by $\frac{n.m - z}{m - z}$ giving the latter.

The limit of esterification is modified but slightly by change of temperature and amounts, in the case of acetic acid, to 62 2 per cent. at 10° and to 66·5 per cent. at 220°.

The esters of monohydric alcohols and monobasic fatty acids are neutral liquids lighter than water (0·8 to 0·9) and pleasant smelling (some forming artificial fruit essences); they are slightly soluble in water (the first members more soluble than the higher ones) and they boil undecomposed.

By means of Grignard's reaction (*see* p. 203), they yield tertiary alcohols

The esters are hydrolysed into their components when heated with alkali, mineral acid, or aluminium chloride, or superheated with water. The mineral acid has a purely catalytic accelerating action on the following reaction due to the water, which is very slow in its action:

$$CH_3\cdot CO_2C_2H_5 + H_2O = C_2H_5\cdot OH + CH_3\cdot CO_2H.$$

With bases, the hydrolysis is expressed by the equation:

$$CH_3\cdot CO_2C_2H_5 + NaOH = C_2H_5\cdot OH + CH_3\cdot CO_2Na.$$

The hydrolysing velocity of acids and bases depends on their degrees of dissociation, *i.e.* on their strengths, so that feeble acids and bases hydrolyse far more slowly than the strong ones. In the case of acids, the hydrolysis is caused by the hydrogen ions, and in that of bases by the hydroxyl ions. In the latter instance, however, the velocity of hydrolysis is greater than with acids, and with methyl acetate, the value of K for decinormal potassium hydroxide is 1350 times that for decinormal hydrochloric acid. In the hydrolysis of fats, the acids of which are feeble and the resultant salts therefore hydrolytically dissociated to a marked extent (*i.e.* even with excess of fatty acid, there always remains free base or hydroxyl ions) complete hydrolysis is obtained industrially with a quantity of base (*e.g.* lime) much less than that required theoretically.

As has been already mentioned, the first ethers of the monobasic acids and monohydric alcohols are, in general, substances of pleasing odour and are used with suitable admixtures as artificial fruit essences.[1]

ETHYL FORMATE, $H\cdot COOC_2H_5$, boils at 55° and is used for artificial *rum* or *arrack*.

ETHYL ACETATE, or Acetic Ester, $CH_3\cdot COOC_2H_5$, is used in medicine and for the preparation of ethyl acetoacetate, which is of considerable importance in organic syntheses. It is prepared by heating alcohol with acetic and sulphuric acids under the conditions given above. It boils at 77° and has the sp. gr. 0·9238 at 0°. Methyl Acetate boils at 57·5° and has the sp. gr. 0·9577.

AMYL ACETATE, $CH_3\cdot COOC_5H_{11}$, is used in alcoholic solution as essence of pears. It boils at 148°.

[1] Commercial *fruit essences* are prepared from the following mixtures of esters, and cost from 2*s.* 6*d.* to 5*s.* per kilo:

Essence of pineapple: 25 grms. ethyl butyrate + 135 grms. amyl valerate + 5 grms. chloroform + 5 grms. aldehyde + 850 grms. alcohol.

Essence of apples: 50 grms. ethyl nitrite + 50 grms. ethyl acetate + 100 grms. amyl valerate + 40 grms. glycerol + 7·5 grms. aldehyde + 7 5 grms. chloroform + 745 grms. alcohol.

Essence of pears: 200 grms. amyl acetate + 50 grms. ethyl acetate + 100 grms. ethyl nitrite + 20 grms. glycerol + 630 grms. alcohol.

Essence of apricots: 35 grms. benzaldehyde + 190 grms amyl butyrate + 10 grms. chloroform + 765 grms alcohol.

Essence of strawberries: 27 grms. amyl acetate + 18 grms. amyl valerate + 9 grms. amyl butyrate + 9 grms. amyl formate + 15 grms. ethyl acetate + 7 grms. essence of violets + 915 grms. alcohol.

Essence of peaches: 100 grms. amyl valerate + 100 grms. amyl butyrate + 20 grms. ethyl acetate + 10 grms. benzaldehyde + 770 grms. alcohol.

ETHYL BUTYRATE, $C_3H_7 \cdot COOC_2H_5$, boils at 121° and is used as essence of pineapple and in rum.

ISOAMYL ISOVALERATE, $C_4H_9 \cdot COOC_5H_{11}$, boils at 194° and is used in essence of apples.

The *higher esters* form constituents of waxes (**Cetyl Palmitate,** $C_{16}H_{31}O_2C_{16}H_{33}$; **Melissyl Palmitate,** $C_{16}H_{31}O_2C_{30}H_{61}$; **Ceryl Cerotate,** $C_{26}H_{51}O_2C_{26}H_{53}$, &c.) These higher esters distil unchanged only in a vacuum; under ordinary pressure they decompose into olefines and fatty acids.

Esters of Polybasic Acids are prepared by the general methods described above: acid esters are obtainable if one or more of the carboxyl groups are not esterified.

The esters of oxalic acid are obtained, for instance, by heating anhydrous oxalic acid with alcohols, the normal ester being separated from the acid ester by fractional distillation.

The importance of **Malonic Esters** in organic syntheses has already been illustrated on pp 308 *et seq*; the normal methyl ester boils at 181° and the ethyl at 198° (sp. gr. 1·068 at 18°). The two hydrogen atoms united with the middle carbon atom can also be replaced by alkyl groups. Thus, for example, **Ethyl Dimethylmalonate,** $(C_2H_5 \cdot CO_2) : C(CH_3)_2$, is obtained from the sodium derivative by treatment with methyl iodide. These compounds, when heated, lose CO_2 and yield alkylacetic derivatives. Similar relations are found with the alkyl derivatives of succinic acid or esters.

The preparation of **Ethyl Acetoacetate** and its importance in organic syntheses have been dealt with on p. 332.

The **Normal Methyl Ester** of succinic acid, $CH_3 \cdot CO_2 \cdot CH_2 \cdot CH_2 \cdot CO_2 \cdot CH_3$, melts at 19° and boils at 80° under 10 mm. pressure; the *ethyl ester* boils at 216°.

GLYCERIDES, OILS, FATS

Glycerol being a trihydric alcohol, its three alcoholic groups may be partially or wholly esterified by acid residues. It suffices, indeed, to heat glycerol with fatty acids to obtain mono-, di-, and tri-glycerides. These glycerides are also formed by the action of the tissues of the pancreas on a mixture of oleic acid and glycerol, a still better method for synthesising fats being the treatment of the sulphuric ethers of glycerol with fatty acids dissolved in concentrated sulphuric acid. Most fats and oils are formed of triglycerides, which, according to the nature of the fatty acid saturating the three alcoholic groups of the glycerol, are termed **Tripalmitin** (melts at 60°), **Tristearin** (melts first at 55° and, after resolidification, at 71·6°), and **Triolein** (liquid, solidifying at about 0°).

Triolein, which is the principal component of liquid fats and especially of olive oil, is formed by the esterification of the glycerol molecule with 3 mols. of oleic acid (*see* p. 298):

$$\begin{array}{l} CH_2 \cdot O \cdot O \cdot C_{18}H_{33} \\ | \\ CH \cdot O \cdot O \cdot C_{18}H_{33} \\ | \\ CH_2 \cdot O \cdot O \cdot C_{18}H_{33}. \end{array}$$

Mono- and di-glycerides are not found in the fats (only ravison oil contains a diglyceride, *dicrucin*; *see also* esters of polyhydric alcohols and glycerol with mineral acids, pp. 213, 222 *et seq.*).

Certain fats (butter, cocoa-butter) contain mixed triglycerides, *i.e.* with different acid radicals, some of them being of acids of low molecular weights,

soluble in water.[1] A. Grun (1906–1909) synthesised mixed glycerides containing three acid residues, all different.[2] The most simple glyceride is Triformin, $C_3H_5(CO_2H)_3$, which was obtained crystalline by P. van Romburgh (1910) by protracted heating of glycerol with 100 per cent. formic acid ; it crystallises with difficulty, melts at 18°, boils at 266° (762 mm. pressure), and at 210°, under ordinary pressure, decomposes. It is hydrolysed slowly by cold water, rapidly by hot.

Oils and fats have coefficients of expansion greater than those of other liquids (100 litres of olein at 0° become 101·6 at 20°).

Fats and, still more, waxes contain also non-glyceride components, *e.g.* **Cetyl Alcohol**, $C_{16}H_{34}O$, which, as such or as palmitic ester, forms one of the principal constituents of spermaceti fat. **Cerotic Acid**, $C_{27}H_{52}O_2$, and its ester occur in large proportions in wax. *Non-hydrolysable substances* (cholesterol, phytosterol, isocholesterol, aromatic alcohols, &c.) are always found in small quantities in fats (olive oil, about 0·75 per cent. ; ravison oil, 1 per cent. ; cotton-seed oil, 1·6 per cent. ; lard, 0·25 per cent. ; cod liver oil, 0·5 to 3 per

[1] *Volatile fatty acids soluble in water.* The number of c c of decinormal potassium hydroxide solution required to neutralise the volatile fatty acids soluble in water from 5 grms. of the fat, constitutes the so-called **Reichert-Meissl-Wollny number** and serves to ascertain the purity of certain fats, especially of butter. The determination is made as follows . exactly 5 grms of the fat (melted at a low temperature and rapidly filtered) are heated in a flask of about 350 c c capacity with 10 c c of alcoholic potash (20 grms of KOH in 100 c c. 70 per cent. alcohol) on a water-bath with frequent shaking until almost all the alcohol is evaporated ; the remainder of the alcohol is completely expelled by shaking the flask and introducing a current of air every half-minute. After about twenty minutes, when the smell of alcohol is no longer detectable, 100 c c of distilled water are added, the heating being continued until a clear solution is obtained (if the liquid does not become clear the test must be commenced anew, hydrolysis being incomplete). To the tepid solution are then added 40 c.c. of dilute sulphuric acid (1 vol. conc. H_2SO_4 + 10 vols water) and a few fragments of pumice the flask being then placed on a double wire-gauze and the liquid distilled, the dimensions of the apparatus being shown in mm in Fig 248 In about half an hour, exactly 110 c c of liquid distil over , this is mixed and filtered through a dry filter 100 c c of the filtrate being titrated with decinormal KOH solution in presence of phenolphthalein. The volume of the alkali used is increased by one-tenth of its value (the volume of the distillate being 110 c c) and diminished by the number of c c of the alkali obtained from a control experiment made without fat as a check on the reagents employed. The result is the Reichert-Meissl-Wollny number. At the present time many laboratories employ the Leffmann-Beam-Polenske method which effects more rapid hydrolysis (*see later*, Butter) For butter the limits for this number allowed by law are 26 to 31·5 (Municipal Laboratory of Milan), the butter being suspected if it gives a value of 22 to 26, although the butter of certain districts and from certain animals may, in exceptional cases, give a number as low as 21. The value for rancid butter, even two months old, is only slightly lower (by about 2) than the normal.

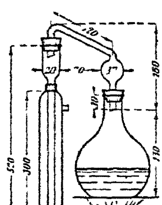


FIG. 248.

Insoluble fatty acids. The quantity of fatty acid insoluble in water obtainable from 100 parts of fat is called the **Hehner number**, and is determined as follows . into a flask of about 200 c c. capacity are dropped, from a weighed vessel containing the dry filtered fat, 3 to 4 grms. of the substance, the vessel being then reweighed exactly After addition of 50 c.c. of alcohol and 1 to 2 grms. of KOH, the flask is heated on a water-bath for five minutes, a clear solution being obtained. If the addition of a drop of water produces turbidity, saponification is incomplete, and the heating is continued for a further period of five minutes, the liquid being then tested as before Evaporation is then continued until there remains a dense mass, which is taken up in 100 to 150 c c. of water, acidified with dilute sulphuric acid, and heated until the clear fatty acids float on the surface. The liquid is then poured on a dry, tared filter (about 12 cm in diameter and in a funnel either without a neck or with a very short one), previously half filled with hot water. The acids are washed with boiling water until the washing water ceases to show an acid reaction (as much as 2 litres of water are sometimes required) The filter is then cooled in a beaker of water so that the fatty acids solidify The filter is then detached from the filter and introduced, with the acids, into a tared beaker, which is heated in an oven at 100° to 102° until its weight remains almost constant (difference between two weighings less than 1 mgrm.). The weight of fatty acids, referred to 100 parts of fat represents the Hehner number.

Unadulterated fats generally have Hehner numbers of 95 to 97 (for butter it is 87·5 , for coco-nut oil, 85 to 92 ; for palm oil, 91)

[2] The synthesis of triolein has been applied practically by G. Gianoli (1891) to diminish the rancidity of oils, especially of *olive oil* obtained from the husks by means of carbon disulphide This oil contains 20 to 30 per cent , or even more, of oleic acid, and is heated in an autoclave with the corresponding quantity of glycerol (or even a slight excess) at 250° in a slow stream of CO_2, or in a vacuum with a trace of oxalic acid to facilitate mixing of the liquids and avoid blackening of the mass owing to the presence of hydroxy-acids ; the distillation of the water formed in the reaction is hastened by adding fragments of tin to the mass. This procedure yields a neutral or almost neutral oil with an iodine number less than 75 and a marked viscosity, so that it can be used even for mixing with lubricating oils. Bellucci (1911) also achieved an almost quantitative synthesis by heating together the theoretical proportions of glycerol (1 mol.) and fatty acid (3 mols.) at 180° to 260° for two hours in a vacuum, so as to expel the water formed, which would otherwise produce the reverse reaction ; in a current of CO_2, the same reaction takes place at the ordinary pressure A. Walter (1911) obtained a mixture of tri- and di-oleins by treating glycerol and acetic acid in presence of the enzymes of castor oil seeds, which act as catalysts. Indeed, *catalysts* cause reversible reactions, and while in presence of water the enzymes of castor oil seeds hydrolyse fats (*see* p. 409) with formation of glycerol and fatty acids, if water is excluded as much as 35 per cent. of the fatty acids can be converted into glycerides.

cent.; tallow, 0·02 to 0·6 per cent.; bone-fat, 0·4 to 2·4 per cent.; wool-fat more than 7 per cent.). The oils of cereals and of *Leguminoseæ* contain abundant amounts of **LECITHIN**, $(C_{18}H_{35}O_2)_2C_3H_5 \cdot PO_4 <^{NH(CH_3)_3}_{C_2H_4 \cdot OH}$, which is decomposed by the enzyme of the pancreas or castor oil seed, but not by that of the blood (*serum-lipase*). The fat of peas contains 1·17 per cent. of phosphorus or 30·4 per cent. of lecithin, and that of wheat, 0·25 per cent. of phosphorus or 6·5 of lecithin; the amount of lecithin is obtained by multiplying that of phosphorus by 26.

Fresh fats and oils contain minimal proportions of free fatty acids (less than 1 per cent.), these increasing with lapse of time, especially if the fats are not melted.

This rancidity is facilitated by sunlight and also by the protein substances of unrefined fats and oils. Coco-nut oil does not readily turn rancid, but with olive oil the proportion of free oleic acid reaches 25 per cent., and with palm oil as much as 70 per cent. of free acids may be formed. The *taste* and *smell* of fats depend, not on the glycerides, but on other substances.

The *specific gravity* of oils and fats varies from 0·875 to 0·970 (*see* Table given later) and is determined by means of an aerometer or Westphal balance (*see* vol. i, p. 73). They are almost completely insoluble in water, acetone, or cold alcohol (this dissolves a certain amount of castor oil and of olive-kernel oil). The solubility increases in boiling alcohol and is complete in ether, chloroform, carbon disulphide or tetrachloride, petroleum or petroleum ether (in the last two, castor oil is slightly soluble, while ether dissolves a little *pure* tristearin).[1]

When heated on a spatula held some distance above a flame, all fats give greenish flames owing to the presence of carbon monoxide and sodium; also all fats are blackened by osmium tetroxide (sensitive reaction).

Oils dissolve small quantities of sulphur or phosphorus and larger quantities of soaps even when they are dissolved in ether or petroleum ether.

The oxygen of the air exerts a marked and rapid influence, as it is fixed by the *drying oils* (linseed, walnut, hemp-seed, poppy-seed, &c.), which are thus transformed into *varnishes*, this occurring more readily if the oils are boiled with oxide of lead or of manganese.

With the other—non-drying—oils, the air (together with light) gradually causes *rancidity*, which, however, some attribute to the action of bacteria, or rather to hydrolysing and oxidising enzymes; however this may be, the acidity increases owing to formation of butyric, caproic, oleic, &c., acids, but the rancid taste and smell are due more especially to the formation of aldehydic, ketonic, and ethereal substances, hydroxy-acids, and volatile acids which can be eliminated by repeated washing with dilute solution of alkali and subsequently of bisulphite (for the aldehydes and ketones, *see later*, Renovated Butter).

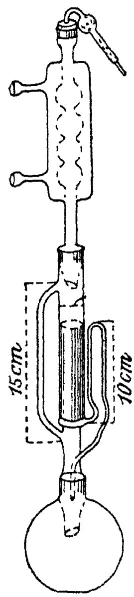


FIG. 249.

[1] To determine the quantity of fat contained in any solid substance, a weighed portion of the latter in a finely divided, dry state (5 to 15 grms. are taken and, if pasty, mixed with fragments of pumice) is introduced into a filter-paper cartridge situate in a *Soxhlet apparatus* (Fig. 249).

The Soxhlet apparatus is connected at the bottom with a tared flask resting on a water-bath, and at the top with a reflux condenser. From 100 to 150 c.c. of petroleum ether or ether are then added and extraction continued for 2 to 4 hours in such a way that the solvent siphons over 15 or 20 times per hour. A calcium chloride tube may be attached to the extremity of the condenser to prevent access of moisture from the air. The solvent is afterwards evaporated from the flask and the residual fat dried at 100° to 102° until almost constant in weight.

The difference between the weight of fat and that of the original substance gives the solids *not fat*.

When fats turn rancid, the *iodine number*[1] is lowered and the *index of refraction*,[2] the *dropping* or *melting point* (*see* pp. 5 and 16), and the *acetyl number* (*see* p. 189) rise. In *butter* rancidity is facilitated by the presence of the casein and milk-sugar, which give rise to other decompositions. Although not rigorously exact, the *degree of rancidity* is expressed by the number of c.c. of normal potash necessary to neutralise 100 grms. of the fat. A *butter* with 10° of rancidity should be rejected. The free fatty acids in fats and oils are usually determined with a decinormal alkali solution, 5 to 10 grms. of the fat being dissolved in 50 to 60 c.c. of a perfectly neutral mixture of alcohol and ether (1 : 2) and phenolphthalein being used as indicator. The *acid number* gives the number of mgrms. of KOH necessary to neutralise 1 grm. of fat.

By passing a current of air through oils heated to 70° to 120°, the so-called *blown* or *oxidised oils*, rich in triglycerides of hydroxy-acids, are obtained. These are dark in colour and have the density of castor oil (but are soluble in petroleum ether), but if " blown " in the cold for a longer time, they are

[1] The Iodine Number is characteristic of a fat (*see* Table, p. 378), and expresses the percentage of iodine absorbed by the fat (*i e.* by its unsaturated components, *e g* oleic acid or the corresponding glycerides, two atoms of iodine being fixed for each double linking, *see* p. 87). This determination requires: (1) An *iodine solution* obtained by mixing, 48 hours before using, equal volumes of the two following solutions: (*a*) 25 grms. of iodine in 500 c.c of pure 95 per cent alcohol, and (*b*) 30 grms of mercuric chloride in 500 c c of pure 95 per cent. alcohol; (2) a *sodium thiosulphate solution*, prepared by dissolving 24 grms of the pure salt in a litre of water, the titre in iodine being ascertained as follows: 3·8657 grms of pure, dry potassium dichromate are dissolved in water at 15° and the solution made up to a litre; exactly 20 c.c. of this solution are introduced into a flask with a ground stopper, about 15 c.c. of a 10 per cent. potassium iodide solution (free from hydroxide) being added and then 5 c c. of concentrated hydrochloric acid This procedure results in the liberation of exactly 0 2 grm. of iodine. The thiosulphate solution is run into this from a burette until the solution is only faintly yellow. A few drops of fresh starch-paste are then added and addition of the thiosulphate continued until the blue colour disappears. It is thus found how much iodine corresponds with 1 c c. of thiosulphate solution, the strength of which remains constant for several months.

The iodine number is determined by dissolving a known weight of the fat or oil (0 2 to 0 5 grm. or, for drying-oils, 0·1 to 0·12 grm.), in a 500 to 800 c.c. flask with a ground stopper, in 15 c.c. of pure chloroform and adding 25 c c. of the iodine solution (prepared forty-eight hours previously, as stated above); if, after two hours, the liquid is no longer very brown, a further measured volume of iodine solution is added and the whole left in the dark. After six hours the excess of iodine left unabsorbed by the fat is determined by adding 20 c c. of a 10 per cent. KI solution, diluting with 150 c c. of water, and adding more KI if the reddish brown solution is not clear. The excess of iodine is then titrated with the thiosulphate solution in the manner already described. Immediately afterwards, 25 c.c. of the iodine solution employed are titrated. The difference between the two values thus obtained, expressed as grammes of iodine per 100 grms. of the fat, represents the iodine number.

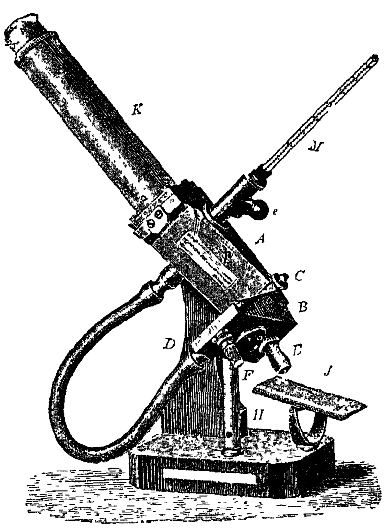


FIG. 250.

[2] The index of refraction is measured in the Zeiss Butyro-refractometer (Fig. 250), by observing the total reflection of a very thin layer of oil or fat situate between two prisms, *p*, mounted in the two chambers, *A* and *B* (the latter rotates on the hinge, *C*, so as to squeeze uniformly the film of oil smeared in *p*; the screw, *F*, fixes *B* against *A*). Indirect light from the sun or from a powerful sodium lamp is passed through the prisms by means of the mirror, *I*, and the limit between the light and dark portions of a scale reading from 0 to 100 is read through the eye-piece, *K*. A thermometer, *M*, indicates the temperature at which the observation is made, and this temperature can be regulated (so as to melt solid fats) by passing water, at a higher or lower temperature, in at *E* and through the rubber tube, *D*, to the outflow, *e*. The refraction is usually stated in the centesimal degrees of the Zeiss scale, the temperature—normally 25°—being indicated Values obtained at other temperatures can be referred to the normal temperature by adding or subtracting 0·55 for each degree above or below 25° (the number 0 55 is accurate for butter, but slightly inexact for other fats).

The *index of refraction* is obtained from the reading on the Zeiss scale by adding to the value 1·4220 as many ten-thousandths as are obtained by multiplying the scale degrees by 7 8 when the reading is between 0 and 30; 7·5 if between 30 and 50; 7 3 if between 50 and 70; and 7·0 if between 70 and 100. (This procedure, too, gives accurate values for butter, but slightly inaccurate ones for other fats). Thus, 30° on the Zeiss scale would correspond with a refractive index of $1{\cdot}4220 + 30 \times \frac{7{\cdot}8}{10000} = 1\,4220 + 0{\cdot}0234 = 1{\cdot}4454$, which agrees almost exactly with the true index of refraction (1 4452); similarly, 60° on the scale means a refractive index of $1\,4220 + 60 \times \frac{7{\cdot}3}{10000} = 1\,4658$. Inversely, the scale reading is obtained by subtracting 1·4220 from the refractive index and dividing the remainder by 7·8, 7·5, 7 3, or 7·0.

The colour of the line of demarcation on the scale sometimes gives an indication of impurity in the fat, being colourless for pure butter, blue if margarine is present, and orange with admixtures of certain other fats.

obtained almost colourless. Blown oils are valued as lubricants. If the blowing is continued, yellow or brown gelatinous masses are obtained. With the exception of the iodine number and the Hehner number—which are lowered—the chemical and physical constants of blown oils (*thickened oils*, &c.) are higher than those of the original oils. Oils also fix *ozone* in proportion to the unsaturated fatty acids they contain, and at the same time become denser (*see* p. 299); olive oil has an *ozone number* of 15·8 (grms. of ozone fixed per 100 grms. of oil, Fenaroli, 1906), maize oil, 21; linseed oil, 33; and castor oil, 16. Also *sulphur* is dissolved and combined in amount increasing with the proportion of glycerides of unsaturated acids present, giving very viscous, brown liquids, sometimes almost solid and gummy.

Chlorine acts on fats, partly replacing hydrogen and partly combining directly.

Iodine is added slowly, but the addition becomes rapid in alcoholic solution and in presence of mercuric chloride (Hubl).

Addition of concentrated **Sulphuric Acid** to oils results in the development of heat and the evolution of sulphur dioxide, in the cold, sulphuric ethers of the triglycerides are formed.[1]

Dilute **Nitric Acid**, in the hot, slowly oxidises fats, while the concentrated acid attacks them with evolution of red vapours.

Nitrous Acid renders non-drying oils denser and solidifies them, the triolein being converted into trielaidin (*see* p. 298); the drying oils remain liquid, although their specific gravity, viscosity, and saponification number increase, and the iodine number and Hehner number (per cent. of insoluble fatty acids) diminish.

When burnt, fats give the characteristic odour of acroleïn, which is derived from the glycerol.

On paper, fats and oils produce a translucent spot, insoluble in water (different from glycerol)

All these reactions serve as qualitative and quantitative tests to establish the purity of fatty substances (*see later*).

WAXES. Unlike fats, waxes are usually composed, not of triglycerides, but of esters derived from the higher monohydric alcohols (*e.g.* cetyl, myricyl, and ceryl alcohols, cholesterol, &c.), and sometimes dihydric alcohols also. They contain, in addition, the high acids (*e.g.* palmitic, stearic, cerotic, oleic, &c.) and alcohols in the free state. Further, beeswax contains as much as 15 per cent. of high melting-point hydrocarbons.

They form homogeneous mixtures in all proportions when fused with fats and give also a greasy spot on paper, but they yield no odour of acrolein when burned (unlike fats) and do not become rancid when exposed to the air.

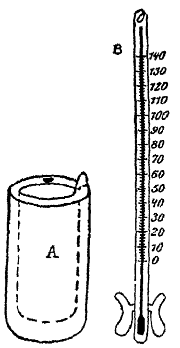


FIG. 251.

The commonest waxes are beeswax, Japanese wax, spermaceti wax (from whales), and carnauba wax (from the leaves of certain palms).

Beeswax forms the hexagonal cells of beehives. After the honey has been expressed, the mass is melted with water to remove impurities; on cooling, a solid layer of crude wax separates at the surface, and this, after melting and casting into blocks, forms *virgin* or *yellow wax*. This is placed on the market in various qualities and colours, some of them being olive-brown; they bear the name of the place of origin and can be bleached with varying facility.

[1] Maumené found that the rise of temperature produced by sulphuric acid of definite concentration serves to distinguish different fats (*see* Table given later). This constant (*Maumené number*) is nowadays determined by means of the *Tortelli thermo-oleometer* (1905). 20 c c. of the oil are poured into the glass receiver, *A* (Fig. 251), the jacket of which has been evacuated. The oil is stirred with the thermometer, *B*, fitted with platinum vanes and the initial temperature read. 5 c.c of concentrated sulphuric acid (sp. gr. 1 8413 or 66° Bé.) are then added from a pipette in thirty seconds, the liquid being kept stirred as long as the temperature rises. The rise of temperature is the *Maumené number*. If the sulphuric acid has not the density given above, but is allowed to absorb even traces of moisture, discordant results are obtained.

The European waxes have the following physical and chemical constants, which allow of the detection of the frequent adulteration to which they are subjected: melting-point, 62° to 64°; solidification point, 60°; specific gravity at 98° to 100°, 0·822–0·847; saponification number, 95 to 97 (rarely 88 to 105); acidity number, 19 to 22; difference between saponification number and acid number (*ester number*), 74 to 76; iodine number, 8 to 11; degrees on the Zeiss butyro-refractometer at 40°, 44 to 45·5 (rarely 42). Foreign waxes have somewhat different constants.

The bleaching of the wax is effected by melting it several times with slightly acidified water, allowing it to cool slowly so as to separate the impurities more thoroughly and then causing it to solidify in thin layers on a cylinder half immersed in water and exposing these to the sun and air for five to six weeks. A more expeditious method of bleaching consists in treatment with hydrogen peroxide or other oxidising agent (dichromate and dilute sulphuric acid), or with animal charcoal. The *white wax* thus obtained—often improved in appearance by the addition of 4 to 5 per cent. of tallow—presents almost the same physical and chemical constants as the virgin wax, the iodine number alone being lowered by 1 to 7.

The wax is insoluble or only slightly soluble in cold alcohol or ether, but dissolves in the boiling solvents. It dissolves in the cold in chloroform, oil of turpentine, carbon disulphide, or fatty oils. It resists dilute caustic alkalis and concentrated alkali carbonates. It is used for making candles, waxed cloth and paper, mastics, artificial fruit and flowers, &c.

Carnauba Wax is exuded from the leaves of certain palms (*Corypha cerifera*) of Brazil and Venezuela. In the crude state, it is hard and brittle, and of a yellowish green colour; it melts at 83° to 88°, has an acid number of 4 to 8, a saponification number of 80 to 95, an ester number of 75 to 76, and an iodine number of 7 to 13, and contains more than 50 per cent. of non-hydrolysable substances. It is used for the manufacture of candles and, mixed with potash (soft) soap, forms the *encaustic* with which pavements are cleaned.

Japanese Wax is the fat extracted from the fruit of certain Japanese and Chinese trees of the order Terebinthaceæ (*Rhus succedanea*, *R. vernicifera*, and *R. sylvestris*). It differs from beeswax in having an ester number of about 200 and a saponification number of about 220. It is completely hydrolysable, since it consists of glycerides of palmitic, stearic, and arachic acids, and contains also 9 to 13 per cent. of free palmitic acid.

STATISTICS. The United States imported 2100 tons (£142,600) of vegetable wax in 1910 and 2200 tons (£199,400) in 1911. In 1900 Italy imported about 1000 quintals of wax, almost all in the raw state, and exported about 1900 quintals of crude yellow and 1100 quintals of white, treated sorts. In 1906, the imports were 1452 quintals; in 1908, 1015 quintals; and in 1910, 1070 quintals (of the value of £14,000). In 1906 Germany imported more than 25,000 quintals of wax and exported more than 4000, besides 10,000 of candles, &c. England imported 3350 tons of wax in 1909 and 3070 tons (£259,049) in 1910. Yellow beeswax costs up to £15 per quintal, and the bleached wax £17.

Hydrolysis (Saponification) of Fats and Waxes. The term saponification is applied to the decomposition of fats into the alcohols and acids composing them, with simultaneous addition of a molecule of water (*hydrolysis*), by heating with water under pressure at 200° or by the action of acid or alkali (*see* p. 371); when alkali is used, the alkali salt (soap) of the fatty acid and not the free acid itself is obtained:

$$\underset{\text{Tristearin}}{C_3H_5(O.OC_{18}H_{35})_3} + 3KOH = \underset{\text{Glycerine}}{C_3H_5(OH)_3} + \underset{\text{Potassium stearate}}{3C_{18}H_{35}O_2K}.$$

The mechanism of the saponification of fats was for long a matter of controversy. Some regarded it as occurring gradually, 1 mol. of fat first reacting with 1 of alkali (bimolecular reaction) (*see* vol. i, p. 67) and di- and mono-glycerides being formed as intermediate products, whilst, according to others, saponification was a single (tetramolecular) reaction. Only since the investigations of Geitel (1897), Lewkowitsch (1898–1901) and, more especially, Kremann (1906), does it appear to be established with certainty that saponification is gradual, consisting of successive bimolecular reactions,

PHYSICAL AND CHEMICAL CONSTANTS OF OILS, FATS, AND THE CORRESPONDING FATTY ACIDS

	Specific gravity at 15°	Solidifying point		Melting-point		Hehner number	Acetyl number	Reichert-Meissl-Wollny-number	Saponification number mgrms. KOH		Iodine number		Maumené number	Butyro-refractometer	Index of refraction at 60°
		Fat	Fatty acids	Fat	Fatty acids				Fat	Fatty acids	Fat	Fatty acids	Fat	Fat	Fatty acids
Vegetable Oils and Fats															
Linseed oil .	0·9315–0·9375	−16° to −27°	13°–17°	−20°	17°–21°	95·5	4–8	—	192–195	197	171–195	179–198	110–126	72·5 at 40°	1·4546
Hempseed oil	0·9255–0·9280	−27°	15°	—	18°–19°	—	—	—	172–192	—	148	141	97	—	—
Poppy-seed oil	0·9240–0·9370	−18°	15°–16°	—	20·5°	95·2	—	—	195	199	133–143	139	86–89	63·4 at 40°	1·4506
Maize oil .	0·9213–0·9255	−20°	16°–14°	—	18°–20°	—	8	—	188–193	198·4	116	119–125	95	67	—
Cotton-seed oil	0·9220–0·9310	—	32°–35°	3°–4°	36°–38°	95–96	8–18	—	193–196	202–208	108–110	111–115	75–90	68·5 at 25°	1·4460
Sesamé oil .	0·9230–0·9237	−5°	21°–23·5°	—	26°–32°	95·7	11·5	1·2	189–193	200·4	103–108	110·4	65	68 at 25°	1·4461
Colza oil .	0·9132–0·9168	−2° to −30°	16°	—	16°–22°	95·1	14·7	0·3	170–179	185	94–102	99–103	55–64	68 at 25°	1·4991
Castor oil .	0·9600–0·9679	−10° to −18°	3°	—	13°	94	147–150	1·4–2·8	183–186	192	83–86	87–93	46·5	78 at 25°	1·4546
Almond oil .	0·9175–0·9195	−10° to −20°	5°–10·5°	—	13°–14°	96·2	—	—	191	204	93–102	93–96·5	52·5	64·4 at 25°	1·4461
Arachis oil .	0·9170–0·9209	−3° to −7°	26°–29°	—	27·7°–32°	95·8	—	—	190–196	201·6	83–100	96–103	45–51	67 at 25°	1·4461
Olive oil .	0·9160–0·9180	−6° to +2°	22°–17°	—	24°–27°	95	10·6	0·3	185–196	193	79–88	86–90	41–45	62·4 at 25°	1·4410
Palm oil .	0·9210–0·9245	—	36°–45°	27°–42°	47°–50°	95	18	0·5	196–202	205·6	51·5	53·3	—	—	1·4510
Palm-kernel oil	0·9520	20·5	20°–25°	23°–28°	25°–28°	87·6–91	2–8	5–6	242–250	258–264	13–14	12	—	36·5 at 40°	1·4310
Grapeseed oil	0·9258–0·9262	—	—	—	—	92·6–93·7	23–25	0·35–0·40	190–195	—	130–140	—	—	—	—
Cacao-butter	0·9500–0·9760	23°–21°	47°–45°	28°–33°	48°–50°	94·6	2–8	1–4	193·5	190	32–41	33–39	—	47 at 40°	1·4220
Coco-nut oil (butter)	0·9115–0·9250	22°–14°	20°–16°	21°–24°	25°–27°	84–90	1–12	7–8·4	246–260	258–266	8–9·5	8·4–9·3	—	34 at 40°	1·4295
Soja-bean oil	0·9255	−18° to −16°	22°	—	27°	95·9	—	0·45	192·9–193·5	—	135	—	86–87	—	1·4750 (at 20°)
Animal Fats															
Ox fat (tallow)	0·9430–0·9520	35°–27°	38°–46°	45°–40°	43°–44°	95·6	3–8	0·25	193–200	197	38–46	41·5	—	49 at 40°	1·4375
Bone fat .	0·9140–0·9160	15°–22°	28°	21°–22°	30°	86–94	11	—	191	200	46–56	55·7	—	—	—
Horse fat .	0·9189	43°–30°	37·7°	37°–43°	37·5°–39·5°	95·5	—	0·3	196	202·6	71–86	84–87	—	53·7 at 40°	—
Butter .	0·9260–0·9400	20°–23°	33°–38°	28°–33°	38°–40°	87–90	2–8	26–28	227	210–220	26–38	28–31	—	41–42 at 40°	1·4370
Hog's fat (lard) .	0·9340–0·9380	27°–30°	39°	36°–40°	43°–44°	93–96	2–6	—	195·4	202	50–70	64	24–27	48–51 at 40°	—
Human fat .	0·9033	15°	30·5°	17·5°	35·5°	—	—	0·3	195	—	61·5	64	—	—	1·4395
Goose grease	0·9274	18°–20°	31°–32°	32°–34°	38°–40°	95	—	1	193	202·4	67–71	65·3	—	50 at 40°	—
Cod liver oil	0·9210–0·9270	0° to −10°	18°–24°	—	21°–25°	95·3	4–8	—	171–189	204–207	167	130–170	102–113	75 at 25°	1·4521
Whale oil .	0·9250	−2°	23·9°	—	27°	93·5	—	0·7–2	188	—	121–136	131	92	70 at 25°	—
Seal oil .	0·9150–0·9300	2°–3°	—	—	22°–24°	95–96	25–34	0·1–0·4	184–196	—	127–141	138–150	92	70–72 at 25°	—

Saponification with lime, baryta, or lead oxide is never so complete as with caustic potash or soda in the hot, while with an alcoholic solution of caustic potash or soda it is complete and rapid, formation of the ethyl ester of the fatty acids and liberation of glycerine first occurring and then complete hydrolysis of the ethyl ester. The latter can be obtained directly from fats by heating with slightly acidified alcohol.

Sodium and potassium carbonates do not attack the fats.

A process has been patented for saponifying fats with sulphur dioxide or bisulphite in autoclaves at 10 to 15 atmos. pressure, or even directly with sodium chloride and ammonia (Garelli, 1907 ; *see later*, Soaps).

Waxes and wool-fat are also saponified, although with less ease, in the same way; with a 2N-alcoholic caustic potash solution and heating under pressure, saponification is, however, complete.

No matter how difficult the saponification of a fat, it can be rendered complete even in the cold by the Henriques process, which consists in dissolving, say, 3 to 4 grms. of the fat in 25 c.c. of petroleum ether and 25 c.c. of normal alcoholic potash, the mixture being shaken from time to time during a period of twelve hours ; on heating, waxes are also dissolved in this manner. To determine the quantity of alkali fixed (*saponification number*),[1] the excess of alkali is titrated with normal acid solution.

Dilution of the saponified waxes with a considerable amount of water results in the separation of the higher alcohols, which can be extracted with ether. Spermaceti contains 40 to 60 per cent. of these insoluble alcohols (which are known industrially as non-saponifiable substances), beeswax 53 per cent., and carnauba wax 55 per cent.

ANIMAL OILS AND FATS

It is not possible here to study in detail all fats, so that only the more important ones, the processes of treating which are partially applicable to the others, will be considered.

Classification of fats into those of animal and those of vegetable origin or into solids (tallow, lard, sheep's tallow, goose grease, and coco-nut butter) and liquids (oils), is of no practical value, but it is necessary, with the liquid vegetable fats, to distinguish between those which have *drying* (linseed, walnut, poppy-seed) from those with *non-drying* properties (olive, colza, arachis, castor, cotton-seed, maize, &c.).

Animal fats are usually melted (by direct-fire heat or by steam) or com-

[1] The Saponification number, or *Köttstorf number*, indicates the number of milligrams of KOH necessary to saponify 1 grm of fat or wax completely The determination is made as follows : 1·5 to 2·2 grm. of the filtered fat is weighed into a 150 to 200 c.c. wide-necked flask, to which is then added 25 c.c. of seminormal alcoholic KOH solution prepared with 90 per cent alcohol and also 25 c c. of neutralised alcohol. The mixture is then heated for 15 to 20 minutes in a reflux apparatus on a water-bath previously heated to boiling, and, while still tepid, is titrated with seminormal hydrochloric acid (not sulphuric acid, which would precipitate K_2SO_4), using phenolphthalein as indicator. Multiplication of the number of c c. of seminormal KOH solution actually consumed in the saponification by 0·0301 gives the number of mgrms. of KOH, which is calculated for 1 grm. of the fat.

Non-saponifiable substances (mineral oils, &c) added to fats as adulterants can be detected by the following qualitative test devised by Holde : two drops of the oil are boiled for one minute with a solution of a piece of caustic potash the size of a pea in 5 c.c. of boiling absolute alcohol, 3 to 4 c.c. of water being afterwards added to the liquid ; in presence of as little as 1 per cent. of non-saponifiable compounds, a turbidity is produced. Also a benzene solution of picric acid gives a red coloration with fat containing 1 per cent. of mineral oil.

For detecting traces of *neutral fats* (non-saponified) in pure *fatty acids* of commerce, *Geitel's test* is employed : 15 c c. of ammonia solution are added to a solution of 2 grms. of the fatty acids in 15 c c. of hot alcohol. Turbidity of the liquid indicates the presence of much neutral fat. If, however, the liquid remains clear, cold methyl alcohol is poured carefully on to its surface ; a turbid ring is formed between the two layers of liquid in presence even of traces of neutral fats (this test does not answer with palm oil).

The *addition of resin* to fat is discovered by the Liebermann-Storch-Morawski test applied to the fatty acids obtained in determining the Hehner number (*see* p. 373) : a few drops of cold sulphuric acid of 50° Bé. are added to a well-cooled solution of 1 to 2 grms. of the fatty acids (which contain the resins) in 1 c.c. of acetic acid. If traces of resin (pine or colophony) are present, an intense red or violet coloration forms immediately and rapidly gives way to a brown fluorescence (presence of cholesterol or wool fat produces a reddish brown coloration, which changes to blue and then to green)

pressed either hot or cold, although sometimes they are extracted with solvents. Vegetable oils are extracted from the disintegrated seeds by pressing them hot or by treatment with suitable solvents. In both cases they are refined by a series of mechanical and chemical operations which will be described more particularly in dealing with tallow, butter, and olive oil.

The statistics are given later for each separate oil, so that here only a few general data are needed: of different fats (with the exception of lard), Italy imported 254,000 quintals in 1906, 197,000 in 1907; 279,000 in 1909; and 232,000 quintals (of the value of £700,000) in 1910, in addition to 5900 quintals of fatty acids (of the value of £16,600). In 1910, England imported 123,150 tons of tallow and stearin of the value of £4,194,484.

TALLOW (ox fat, sheep fat, &c., but not hog's fat) melts at 35° to 37°, contains 75 per cent. of stearin and palmitin (in equal parts) and 25 per cent. of olein. In the crude state, as it comes from the slaughterhouse, it is incorporated in a cellular tissue and contains various impurities, such as blood, skin, &c., which gradually putrefy, giving a bad odour to the tallow. To prepare the real fat from the crude tallow, the latter is cut up in suitable machines fitted with knives and is then melted in open iron or copper boilers provided with stirrers and heated either wholly by direct-fire heat or partly in

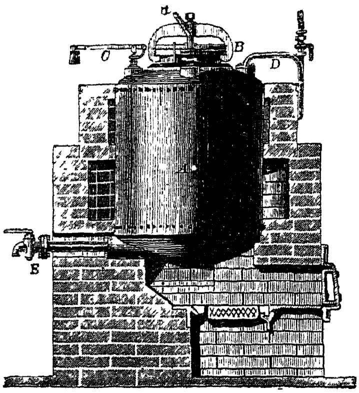


FIG. 252.

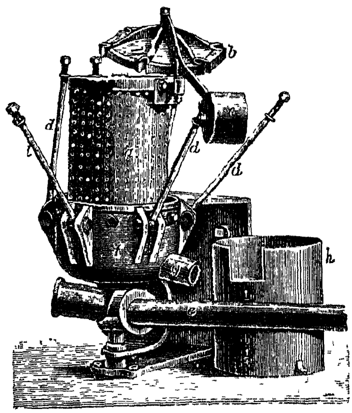


FIG 253.

this way (Fig. 252) and partly by injecting direct steam, superheated to 180° to 200° through the tube, *D*. The strongly smelling gases evolved are led by the pipe, *a*, under the hearth and there burned. The clear, molten fat, after a long rest, is discharged through the tap, *E*, and filtered through a bag, the solid fragments of cellular membranes and other impurities being retained by a perforated double bottom. These impurities, while still hot, are squeezed in a press such as that made by C. E. Rost, of Dresden (Fig. 253), being placed inside the perforated cylinder, *a*, which is surrounded by the jacket, *h*, and closed by the cover, *b*, fixed by the screws, *d*; the pressure is exerted underneath on a plate raised by means of the lever, *e*. The pressed residue is then either treated with carbon disulphide to recover the small amount of fat still retained, or used directly as cattle-food. A powerful press, which is largely used, is shown in Fig 254.

Fusion of Tallow with Acid (d'Arcet method). This method increases the yield and improves the flavour of the tallow, the unpleasant flavour being diminished. It is carried out in the Fouché apparatus (Fig. 255), consisting of a closed boiler, which can be heated both by indirect steam circulating through a coil on the bottom and by direct steam issuing from a perforated pipe passing also to the bottom. 100 kilos of tallow are mixed with 50 kilos of water containing 1 kilo of sulphuric acid of 66° Bé., the whole being heated for two hours at 105° to 110°. The clear, fused fat floats on the surface of the acid solution, which is replaced by pure water, the tallow being heated and mixed with the latter by means of direct steam; after some time, the washed tallow is discharged from a lateral tube—which, inside the vessel, is free and floats—through a cloth bag. When this acid process is used, the solid fragments separated cannot be used for feeding cattle,

Fusion with Alkali. Evrard heats the tallow with a very dilute solution of sodium carbonate, while Rorard treats 1000 kilos of the tallow with 200 of water containing a kilo of caustic soda, the mixture being then melted at 100° in the Fouché apparatus. The alkaline process gives a diminished yield and does not diminish the amount of pungent gases evolved.

Refining. If the fusion, especially when acid is used, has been successfully carried out, refining is usually unnecessary. It is, however, required when the tallow is to be used for food or for fine soaps; that employed for candles is sometimes bleached. In general, it is heated and stirred with water for a long time in suitable vats. It is then left at rest until it separates from the water and is filtered through a cloth bag and collected in a tank, heated outside in order to retard solidification and give time for any further impurities present to deposit.

If the fused tallow is allowed to cool slowly at a temperature above 28°, it sets to a granular mass, as crystals of stearin and palmitin first separate; from this mass the olein is more easily removed by subsequent compression.

Many different processes have been suggested for the *bleaching* of tallow, but the only ones deserving of mention here are those consisting in heating with animal charcoal, bone-black, and fuller's-earth (magnesium hydrosilicate, *see* p. 77 and vol. i, p. 529),

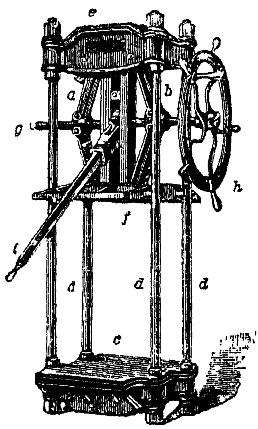


FIG. 254.

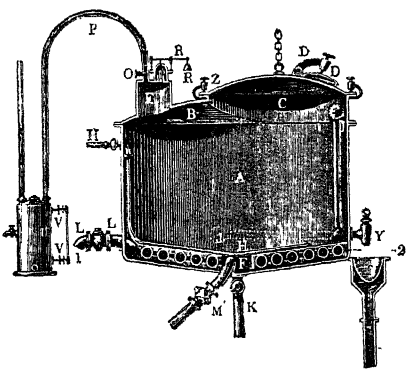


FIG. 255.

and then filtering, and those in which, say, 1000 kilos of tallow are heating with a solution containing 20 kilos of water, 10 of concentrated sulphuric acid, and 5 of potassium dichromate (or 60 kilos of concentrated hydrochloric acid and 15 of permanganate at 40°); after stirring, the mixture is left for a time and then washed several times with hot water. In some cases, the tallow is stirred and heated to 40° with 25 kilos of an aqueous solution containing 250 grms. of potassium permanganate and 250 grms. of concentrated sulphuric acid, and well washed with hot water, a little sodium bisulphite being finally added. Chlorine, which is sometimes used for vegetable oils, is harmful to animal fats. Excellent results have been obtained recently by bleaching with sodium hydrosulphite (vol. i, p. 465). Certain fats can be well bleached at 80° to 100° with 1 to 2 per cent. of barium peroxide, which is added gradually and with continual stirring. Fats and fatty acids are sometimes *deodorised* by treating with 20 per cent. of concentrated sulphuric acid at 30° to 40°, and then distilling the fatty acids under reduced pressure.

The purity of tallow is determined by the analytical methods already given (*see also* Table on p. 378) and for industrial purposes the *solidification temperature* of the fatty acids obtained by the Hehner method (*see* p. 373) is measured by introducing them in the fused state into a double-walled test-tube (best, that of the Tortelli thermo-oleometer, p. 376) and stirring with a thermometer until they begin to turn turbid. The temperature then ceases to fall and at a certain moment rises (the heat of solidification being developed) and remains constant until the whole mass has solidified; this constant temperature is that of solidification and, for good tallow, should be at least 43°. Adulteration with *cotton-seed oil* is detected by *Halphen's reaction*: a mixture of 20 c.c. of

the fat, 20 c.c. of amyl alcohol, and 2 c.c. of a 1 per cent. solution of sulphur in carbon disulphide is boiled in a test-tube ; after about ten minutes heating, a dark orange or red coloration will appear if even as little as 5 per cent. of cotton-seed oil be present. If no coloration is evident after the lapse of ten minutes, a little more carbon disulphide may be added and the heating continued ten minutes longer. If the suspected tallow, or the cotton-seed oil before addition to the tallow, were heated to 200° to 250°, Halphen's reaction would not be given.

The greater part of the tallow made is used in the manufacture of soap and candles, but an appreciable proportion is employed in margarine factories (*see below*). A well-fattened ox may give as much as 100 kilos of crude tallow.

Continental Europe imports large quantities of tallow from America, Australia, and England. The price varies somewhat, and, while in 1870 it was £4 to £5 12*s*. per quintal, in 1884 it was 67*s*., in 1885 56*s*., in 1886 44*s*., in 1888 53*s*. 6*d*., in 1892 49*s*., and in 1893 54*s*. ; in 1906 the price on the Italian markets varied from 56*s*. to 61*s*. 6*d*., in 1907 from 65*s*. to 72*s*., and in 1908 from 60*s*. to 65*s*. 6*d*.

Germany imported 6226 tons of tallow in 1888 and almost 11,000 tons in 1891 (*see later*, Importance of Melted Tallow for Oleomargarine).

In 1909 England imported 110,000 tons of tallow and stearin, and in 1910 123,150 tons (£4,194,484), while the United States exported 8500 tons in 1910 and 22,000 tons (£562,200) in 1911.

OLEOMARGARINE and **MARGARINE (Artificial Butter)**. The oleomargarine obtained from tallow serves to prepare margarine or artificial butter by churning it up with milk. It is also used to some extent for making the so-called *margarine-cheese* from separated milk, the butter being replaced by oleomargarine, which is incorporated by means of emulsors.

It was Napoleon III who, on account of the rise in price of provisions and more especially of butter, offered in 1870 a prize for the discovery of a cheap fat to replace butter, and placed at the disposal of the inventor a large works at Poissy, near Paris, adapted to the development of the industry. The prize was awarded in 1871 to the Mège Mouriès process for the manufacture of oleomargarine from tallow by a method which is almost identical with that used at the present day (the addition of sheep's stomach to render soluble the cellular membranes enveloping the fat has now, however, been abandoned).

As a rule, oleomargarine factories are situated close to the slaughterhouses, so that the tallow may be obtained fresh from the animals. The tallow is cooled immediately by washing it in a current of cold water, which removes the blood and other impurities, and if it cannot be worked at once is hung in separate pieces in a cold chamber.

The tallow is then cut up and introduced, with one-fourth of its weight of water at 55°, into a vat similar to that used for the melting of tallow (*see* p. 380), but nowadays the heating and melting are effected by the circulation of hot water at 60° to 70° instead of steam, so as to avoid scalding the mass. The latter is kept slowly stirred and a couple of hours is sufficient time to melt 2000 kilos of tallow, which floats on the water, whilst the bits and membranes are deposited on the bottom ; this separation is facilitated by the addition of 2 per cent. of salt, previously dissolved in water.

After the mass has remained at rest for some time, all the impurities settle and the molten fat is removed by a tap connecting inside the vat with a free, floating tube which gradually falls as the layer of fat diminishes ; the latter is collected in tinned, double-walled tanks surrounded by hot water, so that further clarification may result on long standing. The fat then bears the name *premier-jus* and is mixed in small proportion into margarine, while the remainder is poured into flat, tinned moulds holding about 20 kilos and allowed to solidify in a chamber kept at a temperature of about 30°.

The semi-solid mass thus formed is placed in cloths and squeezed—not too strongly—in hydraulic presses (similar to those used in making stearic acid for candles, *see later*) in a room at about 25°. This procedure yields about 45 per cent. of a solid residue of stearin (for candles) mixed with a little olein, and a liquid product (55 to 60 per cent.) composed of 55 per cent. of triolein, 35 per cent. of tripalmitin, and 10 to 15 per cent. of tristearin ; this is *oleomargarine*, which assumes an almost pasty consistency at ordinary temperatures and has a yellow colour and a pleasant odour similar to that of butter.

It is used in some cases as fat for cooking, but usually it is converted into artificial butter.

Oleomargarine has the sp. gr. 0·859 to 0·860 at 100°, melts at 33·7°, has the Hehner number (*see* p. 373) 95·5, the Reichert-Meissl-Wollny number (*see* p. 373) 0·4 to 0·9, and the iodine number (*see* p. 375) 44 to 55.

MARGARINE (or **Artificial Butter**) is prepared from oleomargarine, from one-tenth to one-fifth of sesamé or arachis or even cotton-seed oil being added for the lower qualities (in America maize oil is used). In some countries no milk is now used, attempts being made to flavour the oleomargarine directly with certain strongly flavoured cheeses prepared for this express purpose, or with butyric acid or its homologues, or with a special flavouring placed on the market under the name of *margol*.

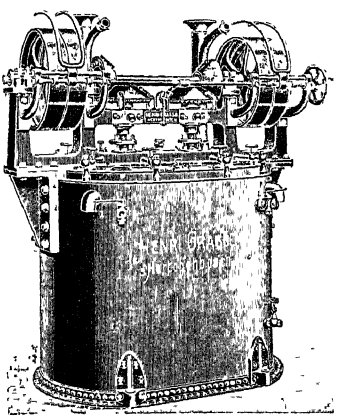


FIG. 256.

It is necessary that artificial butter, when fried, should give the same smell as natural butter, and this result is attained partly by adding a little cholesterol (Ger. Pat. 127,376) to the milk used to render the oleomargarine pasty. Margarine is also required to brown and froth like natural butter when fried, and this is attained by adding about 2 per cent. of egg yolk (Ger. Pat. 97,057) or 0·2 per cent. of lecithin (a constituent of yolk of egg ; Ger. Pat. 142,397) and a small quantity of glucose, while it has also been proposed to add a little powdered casein, egg-yolk and pasteurised milk-cream (Ger. Pat. 170,163).

The yellow colour of commercial, natural butter is imitated by the addition of a little *butyroflavine* (dimethylaminoazobenzene) dissolved in sesamé or cotton-seed oil (placed on the market by the Chemical Factory of Thann and Mülhausen).

In the manufacture of *first-quality margarine*, the fats to be mixed (*e.g.* for summer margarine, 600 kilos of oleomargarine, 30 kilos. of premier-jus (*see above*), and 60 kilos of sesamé oil ; for winter margarine, the premier-jus is replaced by a similar quantity of sesamé oil) are first melted separately at 40° to 45°. For inferior margarines, less oleomargarine, more premier-jus, and a certain amount of cotton-seed oil are used. Half of the molten, homogeneous fat is introduced into a churn (that of H. Grasso, of Hertogenbosch, Holland, Fig. 256, gives good results) containing 300 litres of milk[1] previously churned to the clotting-point and mixed with 50 grms. of colouring solution. The churn has a closely fitting lid and is jacketed so that it can be surrounded with water at 35° to 45° ; it is fitted with stirrers (120 revs. per minute) and the inner surface is thickly tinned. After 10 to 15 minutes churning, the remaining half of the milk and molten fat is introduced, the churning being continued for a further period of 20 to 25 minutes. When the mass has reached a temperature of 30° to 45° (better quality but diminished yield is obtained at 30°), it is allowed to flow into a shallow double-walled vessel cooled by the circulation of water at 0° to 2°, and, as it flows, it is washed with a powerful jet of water at 2° and is constantly mixed with wooden blades. The wash-water is then run off and the hardened, disintegrated mass left overnight so that the wash-water may separate better. A *homogenising machine* of the Schroeder

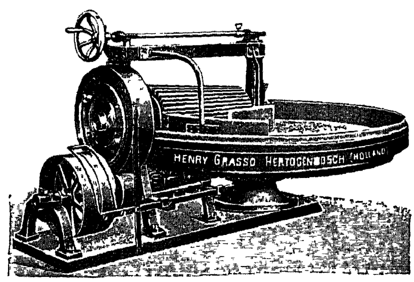


FIG. 257.

[1] For the finer margarines, cream is used, but for ordinary varieties skim-milk from the separators is employed. In all cases, in order to obtain a margarine which will keep, even in summer, the milk is pasteurised at 55° to 60° and then subjected to slight acid fermentation with pure cultures of bacteria, which are sold by butter manufacturers.

The cooled milk is kept in clean, closed vessels in a cool place and is consumed as soon as possible so as to avoid contamination. It may be centrifuged after pasteurising and cooling. If it is not rendered acid, the milk, and also the butter obtained therefrom, keep badly and do not incorporate well with the other fats.

type has been introduced recently, and this allows of continuous working and effects a far more perfect mixing of the fats and milk, while it yields a more aromatic and stable product.

To complete the separation of the whey and washing-water, and to obtain a homogeneous pasty mass, the cold mixture is introduced gradually into an ordinary butter kneader (Fig. 257) with rotating base, this being situate in a cold chamber. After passing under the grooved cone eight or ten times, the mass is collected in blocks, which are left for 24 hours. If it is desired to mix a little cream or the allowed quantity of water (10 to 12 per cent.) into the mass, the latter is introduced into the Werner-Pfleiderer *kneader* (similar to that used for kneading bread), which can easily be reversed so as to expel the excess of liquid and finally the paste itself (Fig. 258).

The margarine thus obtained is made up into cakes by means of suitable moulds bearing the trade mark and is then wrapped in parchment-paper previously disinfected in brine. In some countries this paper is marked with coloured stripes to allow the public readily to distinguish margarine from butter; and in all countries it is obligatory to exhibit margarine for sale in shops with a placard which distinguishes it from butter. In Germany and Austria the law requires margarine to be prepared with at least 10 per cent. of sesamé oil and not more than 10 per cent. of butter; by this means, the detection of butter adulterated with margarine is facilitated, as, owing to the sesamé oil present, it gives the *Baudouin reaction* for furfural.[1] If more than 10 per cent. of butter is added to margarine the Reichert-Meissl-Wollny number (*see* p. 373) exceeds 2·5.

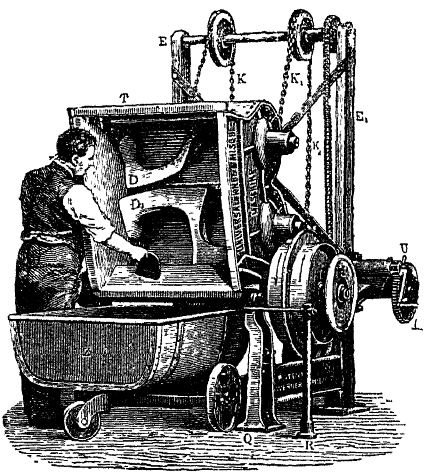


FIG. 258.

Normal margarine contains 8 to 9 per cent. of water and 1 to 2 per cent. NaCl, and has the saponification number 193 to 203 (coco-nut fat raises this number to 220 and the Wollny number to 5) and the iodine number 52 to 60.

The experiments of Lührig (1900) have shown with certainty that margarine is digested by man as well as butter.

The consumption of margarine, which costs little more than half as much as butter, is continually increasing in all countries. Germany possessed 55 factories in 1886 and 83, employing 1555 workmen, in 1895; and in 1899 produced 91,000 tons (worth more than £3,800,000) of first- and second-quality margarines, 55,000 tons of animal fats, 23,000 of vegetable fats and oils, 53,000 of skim-milk, and 4800 of salt being employed. Germany imported 28,500 tons of oleomargarine in 1906 and about 23,000 tons in 1909, and exported 297 tons of artificial butter in 1906 and 525 in 1909. In North Germany, margarine of first quality is used, but in the South margarine without butter and without milk.

In 1907 there were 31 margarine factories in Norway. Thirty-seven factories existed in the United States in 1886, and the output, which was less than 6000 tons in 1902, rose to 45,000 tons in 1908 and 70,000 in 1910 (almost all not coloured), the exports being 1550 tons in 1910 (almost all coloured). In 1910–1911 the output in the United States fell to about 65,000 tons. In Denmark 22 factories produced 30,000 tons in 1909 and 34,300 tons in 1910, when the exports amounted to 1100 tons. England imported 1650 tons of oleomargarine in 1909 and 4050 tons in 1910 and exported 3295 tons in 1909 and 8138 tons (£206,360) in 1910. The principal exportation from the United States consists of the prime material, *oleo oil*, which is largely used in other countries for preparing the different margarines or artificial butters; in 1910, 50,000 tons of this oil (of the value of

[1] 10 c.c of margarine, filtered into a separating funnel, are shaken for half a minute with 10 c.c. of HCl (sp. gr. 1·125). If the acid is coloured red, it is decanted off and the residue shaken with a fresh quantity of the acid. After removal of the acid, 5 c.c of the fat are poured into a graduated cylinder with a ground stopper, where they are shaken with 10 c.c. of HCl (sp. gr. 1·19) and 0·1 c.c. of 1 per cent. solution of furfural in alcohol (absolute) for half a minute. If, after standing, the layer of acid shows an *intense* red coloration, the margarine contained the required quantity of sesamé oil. This reaction has, however, been criticised as being in some cases indecisive.

£2,360,000) were exported, and in 1911, 77,000 tons (of the value of £3,132,600). In 1907, Sweden produced 15 millions of kilos, and in Holland there are over 100 factories. The total output of Holland and Belgium in 1910 was 65,000 tons (of the value of £3,600,000), about 48,000 tons being exported. In Paris, more than 30 tons of margarine were manufactured per day as early as 1875. In Italy, the first factory, that of Regondi and Chierichetti, was erected in 1874 at Milan, with branches in Rome and Tuscany; even in 1888 this firm produced almost 400,000 kilos of margarine, and at the present time, as a company (Chierichetti and Torriani), it still occupies the premier position. A considerable amount of suspicion was removed from the industry in Italy as the result of a valuable report prepared for the Royal Italian Society of Hygiene by Körner and Gabba in 1888, and in 1911 the consumption (largely for adding to butter) reached about 8000 tons; the importation of artificial butter was 121 tons in 1908 and 64 tons in 1910, while the amount exported rose to 216 tons in 1908 and 258 tons in 1910.

Owing to the high price of tallow in recent years, attempts have been made to prepare margarine by the addition of cocoa-butter in the kneader, after complete expulsion of the water (so as to prevent rancidity). There is now on the market margarine which bears the name of *cunerol* (or *kunerol*), and is made exclusively from cocoa-butter, kneaded and treated with a saline solution of yolk of egg (instead of milk). Under the name *buttirol*, L. Annoni prepared, in 1909, an artificial butter by emulsifying oleomargarine or other fat with milk and separating the artificial butter by centrifugation after slight fermentation.

BUTTER is the fat obtained from *milk*,[1] in which it occurs emulsified in small drops, which separate at the surface on standing, or, better, on centrifugation in a separator of the *de Laval* type (Fig 260).

[1] Milk is a liquid secreted by female mammals after parturition, and serves as the first nutriment of the offspring But that of certain animals (cows, goats, &c.) has been largely used, from the earliest times, for feeding infants and adults, and for the preparation of cheese, casein, milk-sugar, &c. The mean daily consumption of cows' milk per head is about 300 grms in England, 450 in Canada, 600 in Holland, 260 in Paris, 600 in Munich, and 150 in London. The supply of milk to large towns constitutes a serious problem, since, for example, Genoa consumes 400 hectols. per day, Turin 600, Milan 1000, Berlin 7400, Paris 8300, and New York 15,000. In 1908 the United States exported £3,200,000 worth of *condensed milk* to China, Japan, the Philippines, Corea, Russia, Africa, and Mexico. The number of cows in France in 1909 was 7,336,000, and the yield of milk 132,000,000 hectols Hungary in 1909 produced 26,000,000 hectols. of milk. In 1903 Australia obtained from 1,300,000 cows about 16,000,000 hectols. of milk, 500,000 quintals of butter (one-third being exported), and 60,000 quintals of cheese (barely one-fifth exported) In the United Kingdom 4,000,000 cows produced in 1909 about 72,000,000 hectols. of milk. In 1910 Norway produced 10,000,000 hectols. of milk.

The *mean composition* of the milk obtained by *complete* milking is found from some thousands of different analyses to be as follows: water, 87·22 per cent.; fat, 3·62 per cent.; nitrogenous substances (casein and a little albumin), 3 66 per cent; milk sugar, 4·82 per cent; and mineral matter, 0·68 per cent. The *casein* forms a kind of colloidal solution, which holds, in an emulsified and suspended condition, fat-drops of varying magnitude (diameter, 0·01 to 0·0016 mm). Casein in milk occurs, indeed, in the form of a non-reversible hydrosol (*see* vol i, p. 105) and its coagulation by acids or heat can be retarded or prevented by the presence of a reversible colloid (*protecting colloid*, like gelatine or gum). In *cows' milk* the relation between casein (non-reversible) and albumin (reversible) is 3 02 . 0 53, whilst in *human milk* this relation is 0·75 : 1·00; in human milk, then, there is abundance of albumin (reversible) and the coagulability is eight times less than with cows' milk. These relations explain the different nutritive effects of the two milks on infants.

Boiled milk can be distinguished from raw milk as it no longer contains reductase or catalase (*see* p. 112); also oxidation of the whey with a little hydrogen peroxide and treatment with pyramidone at 60° yields, with raw milk, a violet coloration, while that of boiled milk gives no coloration. The sugar and, partly, the salts are found in the aqueous solution composing the whey. Milk has an acid and an alkaline reaction (*amphoteric reaction*) at the same time, owing to the presence of primary (acid) and secondary (alkaline) phosphates. The natural acidity of milk is due, not to lactic acid, but to phosphates, carbon dioxide, citric acid, &c.

From milk defatted by centrifugation (*skim-milk*, containing less than 0·3 per cent. of fat), casein for making cheese and for industrial purposes is separated by addition of rennet (from the mucous membrane of the fourth stomach of young calves), which induces clotting owing to the enzyme it contains. Coagulation, with formation of lactic acid (increase from 3° to 15° of acidity), is also caused spontaneously in 24 to 48 hours by adding a dilute acid and keeping at 55° to 60°, the casein probably exists as calcium salt (1·55 per cent. CaO), which is decomposed by acids, the increase in the amount of soluble calcium salts favouring the separation of the casein This casein, separated in the hot and pressed, gradually undergoes fermentation and conversion into **Cheese**. The latter may be either whole-milk cheese or *filled cheese*, prepared from milk the fat of which has been partially or completely removed and replaced by margarine or lard. Copper vessels turn the cheese green on exposure to the air, and to avoid this, all the operations are carried out in vessels of wood, zinc, tinplate, or tinned copper (Besana), although, according to Fascetti, traces of dissolved copper are advantageous in cheese since they retard lactic fermentation; the latter author suggests, however, the addition of hydrogen peroxide, which has the advantages of the copper without its disadvantages. To avoid secondary fermentations during maturation and prevent the swelling and spoiling of the cheese—which otherwise frequently occur—certain selected ferments are initially added under favourable conditions (Gorini, 1905), or attention is paid (Soncini, 1910) to the chemical surroundings in which maturation takes place (*see* p. 126).

In 1906 there were in Italy 3835 dairies employing 15,000 workpeople, and the exports amounted to: butter to the value of £440,000 and 180,000 quintals of cheese; in 1909, 186,500 quintals of cheese were exported, 53,500 being prepared from ewes' milk. The exportation of gorgonzola, &c., was 72,000 quintals in 1907; 66,500 in 1908; 58,900 in 1909; and 78,860 quintals (of the value of £600,000) in 1910. Italy also imported the following

After filtration through cotton-wool or, better, after a brief centrifugation to remove suspended impurities, the milk passes, while still tepid, to the chamber of the centrifuge, *A*, mounted on the axle, *S*, actuated by a pulley which is not shown in the figure (260)

quantities of hard cheese: from Switzerland, 47,400 quintals (and 28,000 from other countries) in 1908, 48,370 (28,700 from other countries) in 1909; and 39,700 quintals (of the value of £320,000) in 1910; in addition to 25,400 quintals (costing about £240,000) from other countries, especially European Turkey.

In 1910 England imported cheese to the value of £6,000,000 (£5,000,000 from Canada alone), and butter to the value of £8,000,000, that from Russia amounting to £3,200,000 and that from Australia to £4,800,000.

Holland produced 790,000 quintals of cheese in 1906, while Hungary imported about 13,000 quintals in 1909

After the cheese has been separated from the skim-milk, further boiling and coagulation of the latter yield the dissolved albumin (*ricotta*), the whey finally remaining being used either as food for calves or pigs or for the manufacture of *milk-sugar* (*see later*, Lactose) Skim-milk is used in some countries for the preparation of cheap and highly nutritious bread or of *kephir* (*see* p. 160), while in recent years it has been utilised for making milk-powder by evaporating it rapidly on a large rotating cylinder of metal heated by steam and in some cases enclosed in an evacuated chamber A knife is arranged to detach the dry powder, which falls into a box The milk may also be concentrated to some extent *in vacuo* and then pulverised with hot air; in some cases the water is removed from the milk by freezing and continual stirring, the residue being subsequently dried Being deprived of fat, this powder does not become rancid, and if a little calcium saccharate is added, it dissolves and gives skim-milk on dilution with water. Milk-powder is also used by pastrycooks. When casein is to be separated for industrial purposes, it is obtained pure by treating the skim-milk at 50° to 60° with a current of sulphur dioxide (Soncini and Todtenhaupt, Ger Pat. 184,300); it is dried in a stream of hot air or, to obtain it in a more soluble state, in a vacuum, while, if a highly pure product is required, it is dissolved in alkali and reprecipitated with nitric acid (it then has the percentage composition: C, 52 96; H, 7 30; N, 15 60; O, 22·54; S, 0 76; P, 0 84). Besides being soluble in alkalis and borax, casein dissolves in solutions of potassium iodide, sodium thiocyanate, sodium phosphate, &c. When dry and powdered, it can be used for certain concentrated food products (*plasmon, nutrose, tropon*, &c), for dressing tissues, for greased paper (rendered soluble with sodium carbonate or borate) and for making material similar to bone or celluloid by compressing it when hot and hardening it with formaldehyde. *Gallatite* and *lactite* are prepared in a similar way.

In 1907 Italy imported 1305 quintals, and in 1910, 1536 quintals (worth £5840), the exportation in this year being 1937 quintals (of the value of £9440). In 1909 Germany imported 28,400 and exported 3950 quintals of casein.

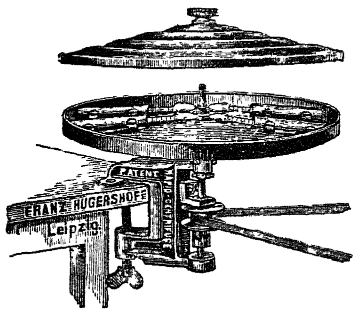


FIG. 259.

ANALYSIS OF MILK Milk being a valuable nutrient for man, and being also easy to adulterate, it is usually analysed chemically to test its genuineness. Milk from cows of different breeds and districts varies within relatively narrow limits, but, in doubtful cases of adulteration, a mixture of the total milk of all the cows of the herd from which the suspected sample is furnished is also analysed. The *specific gravity* is measured with a hydrometer or a Westphal balance at 15° (*see* vol i, p 73 *et seq.*); for natural milk it varies between 1 0295 and 1 0335, and for separated milk from 1·033 to 1·036, while if much water has been added it is below 1 0295. The value of the specific gravity is not sufficient to prove watering, as this value is sometimes maintained unchanged by simultaneous removal of cream and addition of water In such a case, use may be made of the *specified gravity of the whey*, which is never less than 1·027 with pure milk. Watering, even to the extent of only 5 per cent, is also readily detectable by the cryoscopic method examined in 1898 by G. Cornalba (for fresh, non-acid milks free from antiseptics, the cryoscopic point varies from 0 54 to 0·56) or by observing the whey in the Zeiss butyro-refractometer (*see* p. 375). The latter method was proposed recently by Ackermann, who prepares the whey rapidly by clotting 30 c.c. of milk with 0 25 c.c of a calcium chloride solution of sp. gr. 1 1375, heated for fifteen minutes on the water-bath, cooled to 17 5°, and the serum separated by decantation; the reading on the Zeiss scale is 38·8 to 40 for pure milk, 37 7 for milk + 5 per cent of water, 36·7 with 10 per cent., 34 8 with 20 per cent., 33·3 with 30 per cent., 32 with 40 per cent, &c. G Cornalba (1908) holds that genuine milk contains at least 6 per cent. of *soluble substances* (*i.e* dry residue less fat and casein), every 0 2 per cent less than this amount indicating 5 per cent. of added water. Since natural milk does not contain nitrates, which are, however, present in nearly all waters, *watering* can also be detected by testing the milk for nitrates in the same way as wine is tested (*see* p. 157). Watered milk appears slightly blue when compared with genuine milk.

The *total residue* and *ash* are determined by evaporating 5 grms. of milk with a drop of acetic acid in a platinum dish, drying in an oven at 105°, and weighing; the dry residue thus obtained is then heated to redness until completely incinerated and weighed; the ash is used for the detection of borax or sodium bicarbonate.

Genuine milk has not less than 12 per cent. of dry residue, or, subtracting the amount of fat, not less than 9 per cent. The dry residue (r) may also be calculated from the specific gravity (s) and the percentage of fat (g) by Fleischmann's formula: $r = 1{\cdot}2g + 2{\cdot}665\,\frac{100s-100}{s}$.

Determination of Fat. This is usually made with the *Gerber butyrometer* (Fig. 259) Into a special wide-mouthed flask with a long, narrow, graduated neck are pipetted 10 c.c. of concentrated sulphuric acid (sp. gr. 1·825), 1 c.c. of amyl alcohol, and 11 c.c. of milk, which are allowed to flow gently down the side. The flask is then tightly closed with a rubber stopper, wrapped in a cloth and shaken rapidly and vigorously, the flask with the pink or red liquid is immersed for six or seven minutes on a water-bath at 65° to 70° and then centrifuged on a flat plate, being arranged radially in clips with the mouth towards the circumference. After a few minutes centrifugation, the fat is separated from the acid casein solution and the percentage of fat by weight is read off on the graduated neck of the flask after the latter has been left for a few minutes on the water-bath.

The official method—which is used rarely and only in cases of dispute—of estimating fat is that of Soxhlet, and is based on the density of the ethereal solution of the fat extracted from the milk after rendering alkaline. In nearly all countries it has been established that a natural milk, obtained by milking completely a number of cows, contains as a rule not less than 3 per cent. of fat, in very rare cases 2·9 per cent., and more frequently 3·5 per cent.

If the specific gravity (s) and the dry residue (r) of a milk are known, the fat (g) that it should contain is deduced from Fleischmann's formula: $g = 0\,833\,r - \frac{2\,22\,(100\,s - 100)}{s}$.

and which rotates several thousands (6 to 7) of times per minute. In this manner the skim-milk is expelled to the periphery and carried off by the tube, *b*, into the collecting plate, *Bc*, whilst the lighter cream rises and is discharged by the channel, *e*, into the collector, *Cf*. These separators easily treat 10 hectols. of milk per hour. The cream that separates is agglomerated into small lumps of butter by churning (*see*, for instance, Fig. 256, on p. 383), kneading, and so on, just as with margarine. To obtain a butter that will keep, however, the cream is subjected to pasteurisation and acidification (*see* Note on p. 383), the butter being worked with water that has been sterilised, for instance, by ozone or ultra-violet rays. The flavour of butter, which was formerly regarded as due to the esterification of the fatty acids, seems to result from the fermentation of lactose and the formation of aldehydes.

The proportions of the various fatty acids entering into the composition of the glycerides of butter are as follow: stearic, 7 to 11 per cent.; palmitic, 14 to 18 per cent.; myristic, 11 per cent. or more; lauric, 14 to 16 per cent.; oleic, 25 to 30 per cent.; higher unsaturated acids, 4 to 5·7 per cent.; also the volatile acids, butyric, caproic, caprylic, and capric; further, small proportions of acetic, arachic, and hydroxy-acids, cholesterol, phytosterol, lecithin, and a yellow colouring-matter; winter butter is less yellow than that of summer (green feeding of the cows). Unlike other fats, butter contains a mixed palmito-oleo-butyric glyceride, $C_3H_5(C_{16}H_{31}O_2)(C_{18}H_{33}O_3)(C_4H_7O_2)$.

Also, in comparison with all other fats, butter contains a large quantity of volatile acids soluble in water.

Commercial butter should contain not more than 18 per cent. of water (or 16 per cent. + 2 per cent. of salt) and at least 80 per cent. of pure fat.

In judging of the purity of butter, reference should be made to the constants given in the Table on p. 378 and to what has been said on pp. 373 and 375 with respect to the soluble volatile acids and to the butyro-refractometric reading, which should have the following values at different temperatures: 41·5 at 45°, 43·6 at 43°, 43·7 at 41°, 44·7 at 39°, 45·9 at 37°, 47 at 35°, 48·1 at 33°, 49·2 at 31°, 50·3 at 29°, 51·4 at 27°, and 52·5 at 25°.

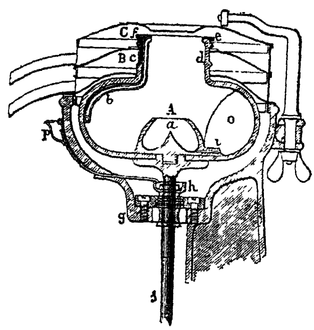


FIG. 260.

The most certain method of detecting adulteration of butter with *coco-nut oil* is by determining the volatile fatty acids *insoluble in water* (Polenske number).[1]

Adulteration with *margarine* is readily detected by the content of aggregated crystals which are observed under the microscope in polarised light or, better, in light which has previously passed through a selenite plate. Fresh, non-melted butter does not, indeed, yield crystals, but old and rancid or melted butter does give them, so that, in this case, the test is invalid.

The determination of *water*, fat, solids not fat (casein, lactose, and mineral salts) can be simply carried out, according to Fahrion (1906), as follows: in a platinum crucible, tared together with a glass rod, are weighed 2·5 to 3 grms. of butter, which is then heated over a small flame and stirred until it is melted and clear; reweighing gives the proportion

[1] Polenske (1904) showed that coco-nut oil contains a high and constant proportion of volatile fatty acid *insoluble in water*, whilst butter contains very little of these. If the Polenske number (or *new butter-value*) is expressed in c.c. of decinormal KOH necessary to neutralise the insoluble volatile acids contained in 5 grms. of the fat, its value is 16·8 to 17·8 for coco-nut oil and 1·5 to 3 for pure butter. The Reichert-Meissl-Wollny number and the Polenske number may be determined by a single operation, the butter being saponified in the following manner (Leffmann and Beam): 5 grms. of the filtered butter, together with 20 grms. of glycerine and 2 c.c. of caustic soda solution (100 NaOH to 100 H_2O), are placed in a flask of about 300 c.c. capacity, this being heated with a naked flame. After 5 to 8 minutes boiling, the water evaporates, frothing ceases, and the mixture becomes clear, the heating being then continued for a few minutes longer. When the liquid has cooled to 80° to 90°, 90 c.c. of water at 80° are added, a clear and almost colourless solution of the soap formed being thus obtained. To this solution, heated nearly to boiling, are added 50 c.c. of dilute sulphuric acid (25 c.c. of the concentrated acid in a litre) and ½ grm. of powdered pumice, the volatile acids being then distilled so that 110 c.c. are collected in 19 to 21 minutes in an apparatus corresponding exactly with that shown in Fig. 248 on p. 373.

The 110 c.c. flask is cooled in water at 15° and inverted several times to cause the drops of insoluble fatty acids to collect. The liquid is filtered, titration of 100 c.c. of the filtrate with decinormal KOH giving the Reichert-Meissl-Wollny number. The tube of the condenser and the 110 c.c. flask are then washed with three separate amounts of 15 c.c. of water, which is passed through the filter, the flask being subsequently washed with three quantities, each of 15 c.c., of neutralised 90 per cent. alcohol. Titration of the whole of the alcoholic filtrate with decinormal KOH gives the Polenske number, which allows of the detection of 10 per cent. of coco-nut oil in butter. The result has been stated to be inconclusive if the cows have been fed with coco-nut cake.

of water. The residue is then dissolved in light petroleum and the solution filtered through a tared filter, which is well washed with solvent. The filtrate is distilled in a tared flask and the remaining fat dried for an hour in an oven at 100° to 102° and weighed. After drying at 100° the weight of the filter less the tare gives the non-fat. By burning the filter in the crucible, incinerating and weighing, the salts (NaCl) or mineral substances are obtained.

The *degree of rancidity* is determined as described on pp. 374 and 375.

In order to avoid rancidity, butter must be kept or despatched in ice or in cold chambers. Butter may be coloured yellow by saffron, tumeric or, more commonly, *annatto*, which is an extract of the fruit of *Bixa orellana* made into a paste with an oil ; the use of coal-tar dyes is prohibited.

No addition of antiseptic, for the keeping of butter, is allowed ; boric and salicylic acids can be detected as in beer (*see* p. 179). The presence of formaldehyde may be ascertained by distilling 25 c.c. of water in a current of steam from a flask containing 50 grms. of butter and 50 c.c. of boiling water ; the distillate is tested by means of Rimini's reaction (*see* p. 109).

Addition of artificial yellow colouring-matter is shown by the intense coloration assumed by absolute alcohol when shaken with the fused butter.

The price of butter varies with the year and season from about 2*s.* to 2*s.* 9*d.* per kilo.

Italy produced more than 220,000 quintals of butter in 1906 and has always been a large exporter, but the competition of other countries (Russia, Denmark, &c.) and the severity with which England, in particular, penalises sophisticated butter have diminished the exports from 60,000 quintals in 1905 to 50,000 in 1906, 35,000 in 1907, 31,840 in 1908, and 34,000 in 1910. While at one time the amount exported annually to England was as much as 30,000 quintals, it was only 5000 in 1907, 6800 in 1908, and 8500 in 1910.

In 1906 Russia exported 432,323 quintals of butter and in 1907 547,000 quintals. 260,000 of this quantity being from Siberia alone. England imported butter to the value of £21,000,000 in 1904. In 1902 the United States produced 6,000,000 lb. of *renovated butter*,[1] in addition to margarine and ordinary butter. In 1909 Germany imported 104,000 quintals of butter from Russia and 168,000 quintals from Holland. Hungary produced 200,000 quintals in 1909 and Holland 600,000 in 1906.

BONE FAT is obtained mainly from glue factories, and is extracted from the crushed bones either by boiling with water (*see* vol. i, p. 508) and skimming the fat which collects at the surface, or by treatment with benzine or carbon disulphide in an extraction apparatus (*see later*). The first method yields 3 to 4 per cent. of fat, and the second 7 to 9 per cent. The latter has, however, an unpleasant smell and is dark and of inferior quality ; it can be refined by means of dilute sulphuric acid or sulphuric acid and dichromate or barium peroxide (*see* Tallow). Its constants are given in the Table on p. 378.

It is used in making soap, especially resin-soap.

HOG'S FAT (Lard) is obtained by melting the fatty parts of the pig, as in the case of tallow (Refining, *see* p. 381). In Germany large quantities of it are consumed for culinary purposes, and in Italy almost the whole of this product is used by the lower classes as a substitute for butter and oil. Considerable amounts are employed in making soap and candles. In 1891 Germany imported 750,000 quintals from the United States ; but since this was prepared with all the refuse of oxen and pigs, and also with the residues of diseased animals, while addition of appreciable quantities of cotton-seed oil and bleaching by the addition of lard stearine were also resorted to, the food-value was greatly lowered. In 1906 Germany imported a total of 1,251,152 quintals of lard, of the value of £4,600,000. The Table on p. 378 gives its constants. The presence of cotton-seed oil is detected by Halphen's test (*see* p. 381).

In the United States the production of lard is continually increasing, 21 millions of pigs being killed in 1902 and 25½ millions in 1905, the exports amounted to 170,000 tons (£9,187,200) in 1910 and 270,000 tons (£10,901,000) in 1911. Italy imported 9934 quintals of lard in 1906, 17,520 in 1907, 21,700 in 1908, 23,849 in 1909, and 10,564 quintals (worth £63,400) in 1910.

[1] *Renovated butter* is prepared in America from rancid butter, which is kneaded with a solution of sodium bicarbonate (*e g.* in the Werner and Pfleiderer kneading machine, Fig. 258, p 384), and is then washed with just tepid water in the rotating-plate kneader (Fig. 257, p. 383) until it no longer gives an alkaline reaction. It is then kneaded again in the former machine with milk, cooled with a jet of very cold water and treated like ordinary butter a second time in the latter kneader. Natural butter can be distinguished from renovated butter since when melted at a moderate temperature, the former gives a limpid and the latter a turbid mass.

FISH OILS: WHALE OIL and COD-LIVER OIL. The fat of the whale, seal, and dolphin is extracted from a species of lard contained in the membranes of the brain and back; it is, however, worked in a primitive manner, being left to melt and putrefy in barrels exposed to the sun. The oil being thus separated, the residue is boiled with water to extract the tallow. When heated with water, the oil loses its unpleasant odour to some extent.

The head and other parts of the body of certain whales, especially *Physeter macrocephalus* (Cachelot whale), contain an oil already separated and different from that of the lard; it solidifies at the ordinary temperature, giving the so-called **SPERMACETI** (or **Sperm Oil**), which, after filtration, pressure (to separate the stearin or solid wax), boiling with water and a little caustic soda and repeated washing with water, forms a fat or oil of great value in the manufacture of pharmaceutical products, perfumes, and high-class candles.

Cod-liver Oil (from the fresh liver of *Gadus morrhua*, caught in large numbers in Norway and elsewhere) is used in considerable quantities as a recuperative medicine in virtue of the small proportion of chemically combined iodine and of the large amounts of readily emulsifiable fatty acids it contains. It is now obtained with a less unpleasant taste and smell, as it is being prepared in a more rational way by melting it in closed vessels with hot water or direct steam, the best results being obtained in absence of air—in an atmosphere of hydrogen or carbon dioxide or in a vacuum (Eng. Pat. 25,683, 1906); it is then freed from the stearin by thorough cooling and filtration.

Natural cod-liver oil, prepared by the old process, has a considerably higher acidity (acid number, 8 to 25) than that separated by the more modern methods (acid number, 0·7 to 1·4).

The production of cod-liver oil in Norway shows a continual increase, although it varies in different years, according to the abundance or scarcity of the fish, from 20,000 to 100,000 tons per annum, about one-half of this amount being obtained by the newer methods of extraction. Italy imported 31,170 quintals of fish oil in 1906, 55,036 in 1907, and 61,323 quintals (of the value of £122,686) in 1910. Germany imported 213,400 quintals in 1909.

Adulteration of the oil is detected by analysis, taking account of the constants given in the Table on p. 378.

Fish-oil Waste is used in dressing leather, in the manufacture of **DÉGRAS**,[1] also employed for treating skins, and in the preparation of fatty acids for soap-making; these fatty acids are *deodorised* by heating with 15 to 20 per cent. of concentrated sulphuric acid at 30° to 40°, washing and distilling with superheated steam.

WOOL FAT. Pliny mentions the use of this fat in medicine and its employment for this purpose extended to the seventeenth century. In 1856 Chevreul classified it with the waxes

[1] **DEGRAS** is obtained in the *chamoising* process (separation of the fat from the skins after it has served to oil them during tanning) and is used for tanning other skins. It consists essentially of water (30 to 40 per cent.), rancid fish oil, resinous substances (*dégragène* or *dégras-former*, 14 to 20 per cent.) from the oxidation of the oil, mineral substances (about 2 per cent. consisting of lime, soda, and sulphates) and residues of skin, membranes, hair, &c. (about 5 per cent.). It has an acidity number of 25 to 35, an iodine number of 34 to 36, a saponification number of 144 to 155, an acetyl number of 32 to 44, and 1 to 3 per cent. of non-saponifiable substances. It is yellowish brown, has an odour of fish oil and readily forms a very persistent emulsion with water. *Dégragène* is the characteristic constituent and, unlike other resins, is insoluble in light petroleum.

Its value in dressing skins lies in its property of penetrating readily, and in large quantities, the *semi-moist* skins, in the pores of which it becomes uniformly distributed, imparting very desirable softness and fullness, as well as keeping qualities.

This use of dégras has been known for many years and has increased so rapidly that the supply is no longer sufficient, factories for *artificial dégras* having been established. This is prepared by kneading refuse and clippings of skins with fish oil, exposing the mass to the air to oxidise and pressing out the artificial dégras or *moellon*; the residue is then treated with a fresh quantity of fish oil, this operation being repeated until practically no residue remains. Attempts have also been made to obtain moellon by pulverising fish oil in the air at 120° and emulsifying with water. At the present time, the term *dégras* is applied to a complex substance for dressing skins and consisting of a mixture of moellon with wool fat, tallow, and other solid fats, whilst by moellon is indicated the aqueous emulsion of oxidised fish oil. Artificial dégras is now preferred to the natural product, since different types can be prepared for different purposes, such types being of more constant composition, and hence more certain in their effects. A good artificial dégras usually contains 15 per cent. or more of dégragène and less than 20 per cent. of water. When such dégras contains more than 1 to 2 per cent. of non-saponifiable substances, these are derived, not from the fish oil but rather from the wool fat, resin oil, mineral oil, &c. French dégras sometimes contains 1 to 2 per cent. of soap and as much as 5 to 6 per cent. of skin fibres: in general, it should contain less than 0·05 per cent. of iron and, when spread in a thin layer on glass and kept for ten hours in an oven at 100°, it should not form a varnish but should assume only a horny consistency. When smeared on moist and well-pressed paper, it should be absorbed within an hour, leaving only a minimal residue.

Natural dégras costs about 56*s*. per quintal, the artificial product of the first quality about 40*s*., and the French (moellon) about 68*s*.

owing to its richness in cholesterol, and in 1867 Vohl proposed its preparation from the wash-waters of wool. When washed with tepid water, soap, and a little potassium or ammonium carbonate, certain greasy wools (from Australia) lose as much as 40 to 50 per cent. of their weight as soil, fatty acids, potash soapy substances and fat, secreted by the superficial layers of the skin. The wool from certain races of sheep may contain from 7 to 35 per cent. of true fat (if the sheep are not washed before shearing).

In some factories the wool fat is extracted from the dried wool by means of carbon disulphide or, better, of benzine (at Verviers, in Belgium, the wool from all the establishments in the city has for several years been washed with benzine in a large works), subsequent washing with water and a little soap being then more easy and economical. The *crude fat* obtained in this way after distillation of the solvent is slightly coloured and almost free from water, and is ready for the market. Usually, however, the dirty wool is washed in the Leviathan machine, the soapy, greasy wash-waters being first allowed to stand to deposit earthy matters and then treated with dilute milk of lime or, better, with calcium chloride solution slightly acidified with hydrochloric acid. The soaps and fatty acids (palmitic, cerotic, a little caproic and oleic and traces of stearic, isovaleric, butyric, myristic, carnaubic, and lanoceric) are precipitated as calcium salts and carry down the *wool fat*, which is only slightly saponifiable owing to its large content (55 to 60 per cent.) of cholesterol, isocholesterol, ceryl alcohol, lanolyl alcohol ($C_{12}H_{24}O$) and carnaubyl alcohol ($C_{24}H_{50}O$), which do not contain glycerides. After this treatment the wash-waters are either left to stand or coarsely filtered to separate the pasty mass; in some cases the water is removed from the calcium soap and fat by centrifuging in a separator similar to that used for milk (Fig. 260, p. 387). The paste thus obtained is *dried* in the sun or in an oven and then made into cakes with sawdust, &c., the rather dark *crude wool fat* being extracted from these by means of carbon disulphide or, better, benzine. The residue from the cakes, when treated with dilute sulphuric acid, yields fatty acids and the resultant aqueous emulsion, coarsely filtered to remove solid substances, deposits the fatty acids on heating.

Thus obtained, wool fat is dirty yellow, transparent, and very viscous (it can be obtained pale yellow by special refining processes); it melts at 35° to 40°, and has a saponification number of 85 to 105, an iodine number of 13 to 17, an acid number of 0·5 to 1·3, a Hehner number of 85 to 95, a Reichert-Meissl number of 6 to 7, and 0·5 to 1 per cent. of water, while its rotatory power in saccharimetric degrees is +10·2 to +11·2. Commercial lanoline does not contain more than 30 per cent. of water.

Wool fat is better suited than any other fat or even vaseline as a basis for salves and ointments, and has also considerable power to penetrate the skin. It mixes readily with large proportions (up to 105 per cent.) of water (which separates in the hot) and, if mixed with 20 per cent. of olive oil, it can absorb 320 per cent. of water.

In some cases the crude wool fat is distilled with superheated steam, this procedure giving a *wool oil* or *wool oleine* containing 40 to 50 per cent. of fatty acids, 35 to 45 per cent. of hydrocarbons, and 5 to 10 per cent. of alcohols, while the distillate deposits a *wool stearine*, which melts at 42° to 55°, has an iodine number of 37, and a saponification number of 170, and contains cholesterol and, altogether, 73 to 88 per cent. of free, solid fatty acids.

In 1905 Germany exported 1340 quintals (1300 in 1903) of lanoline, of the value of £10,000.

VEGETABLE OILS

In plants oils accumulate especially in the seeds and the fleshy parts of the fruit, rarely in the roots. The composition of these oily parts varies somewhat with the locality and with the character of the season.[1]

In 1881 Italy imported 201,000 quintals of vegetable oils for industrial purposes; in 1891 about 542,000 quintals, and in 1903 almost 707,000 (20,000 of palm and coco-nut and 43,000 of cotton-seed oil; in 1905 the amount rose to 120,000 quintals) In 1905 Italy also imported 650,000 quintals of oily seeds (104,000 of castor oil, 180,000 of sesamé and arachis, and 360,000

[1] For the Mean Composition of Oily Seeds and Fruits (the maxima and minima are 10 to 15 per cent. above and below the mean values), *see* Table at foot of next page.

of linseed, rapeseed, and ravison). In 1910 Italy imported 58,456 quintals of olive oil, 3825 of linseed oil, 35,800 of cotton-seed oil (in 1909, 306,000 and in 1908, 108,000 quintals, of the value of £320,000), 20,000 of coco-nut oil, 81,900 of palm oil, 177 of castor oil, and 50,800 (only 4700 in 1908) of arachis oil; in the same year were imported also 129,570 quintals of castor oil seeds, 367,660 of linseed (463,000 in 1909), 22,800 of rape and ravison seeds, 385,880 of sesamé and arachis seeds, and 130,000 quintals of various other oily seeds. In 1908 France imported 7,830,400 quintals of oily seeds (4,650,000 for Marseilles), and 324,000 quintals of olive oil. The imports at Marseilles alone were, in 1910, 6,656,790 quintals of oily seeds, 348,000 quintals being arachis, 171,423 tons copra, 91,000 tons sesamé, and 11,655 tons cotton-seed.

The oil is extracted by two processes: *by pressure* and *by means of solvents*. Edible oils are always obtained by the former method, as also are most of the others, solvents being used to extract the remaining oil from the pressed residues (*oil-cake*), when these are not to be used for cattle-food.

According to the power and degree of perfection of the pressing appliances, from one-fourth to one-seventh of the total oil is left in the cake. Extraction of the powdered cake with solvents removes all but the fiftieth part of the total amount of oil (1 to 2 per cent. instead of 10 to 12 per cent.).

The seeds are not worked up immediately after gathering, but are first matured, dried, and turned in bins or silos. They are then cleaned with sieves and fans, crushed in a kind of roller press (similar to that shown in Fig. 212, p. 251) and powdered (sometimes this is done directly) in vertical cast-iron or stone mills like that illustrated in Fig. 210 on p. 251. A mill with a diameter of 1·7 metre converts about 35 litres of linseed into flour in twenty-five minutes.

To obtain the edible and so-called virgin oil, the flour is pressed cold, although more commonly the pressing is carried out in the hot, this increasing the yield but injuring the quality and colour.

	Water	Ash	Oil	Organic matter free from oil	Proteins in 100 parts of organic matter	Cakes after pressing	
						Fat per cent.	Protein per cent.
Olive: pulp	24·22	2 68	56 40	16·70	1·10		
kernel (shell)	4·20	4 16	5·75	85 89	2·50	5–15	4–8
seed	6·20	2 16	12·26	79 38	2·16		
Linseed winter	8·65	3·15	35·20	53	22 10	6–8	30–38
summer	7·80	3 20	31·60	57·40	24		
Ricinus (seeds): Italian	8	2·93	52·62	36 45	25·50	7–10	28–31
Indian	7 26	3·40	55·23	34·11	24·26		
Sesamé (seeds): brown Levant	5 90	7·52	55·63	30·95	21·42	10–15	35–40
yellow Indian	7 06	6 85	50 84	35·25	22·30		
Cotton-seed: Egyptian	7·54	8 60	23·95	59·91	27·20	12–16	36–48
American	8·12	9·44	20·58	61·86	28·12		
Colza or rape (seeds)	6	4·30	38	51·70	20	8–10	29–32
Ravison (seeds): fresh	9 10	4 80	36 80	49·30	2 50	7–10	29–32
two years old	5 25	4·36	39·25	51·14	4 20		
Arachis (shelled nuts): fresh	7·37	2·43	37 84	52·36	27·25	6–9	44–50
old	2 75	2·50	41·63	53·12	27·85		
Hempseed	8·65	3 45	33 60	54 30	15·95	8–12	28–33
Mustard: black	6 78	4 21	22 20	66 81	20 52	—	—
white	7	4·45	29·30	59·25	28 20	—	—
Poppy. white	8 85	3 42	55·62	32·11	16 89	9–11	33–37
black	9 50	4	51 36	35 14	17·50		
Sweet almonds	9·53	2·86	51·42	38·19	22·50	—	—
Maize: whole grain	—	—	6·10	—	—	—	—
germ	—	—	44 46	—	—	6–10	14–18
Palm fruit	—	—	65·72	—	—	—	—
Palm kernel	—	—	45·50	—	—	7–9	14–17
Coco-nut	—	—	45·63	—	—	10–14	18–22

Nowadays the pressing is effected almost everywhere with hydraulic presses of various forms,[1] and only in small works are wooden or metal screw-presses still employed.

A hydraulic press which is widely used is the ring-press of Brink and Hübner, of Mannheim, shown in Fig. 261. The powdered seeds are placed on the rings, *a*, the base of which consists of a movable, perforated steel plate covered with a disc of woollen or horsehair material. The flour is well pressed by hand or by a suitable machine, covered with a second woollen or horsehair disc, and passed along the guides, *b*, being thus brought between two plates, *e*, which are smooth underneath and grooved on the top and fit exactly into the two rings containing the flour, one above and the other below. The grooved side of the plate has also a circular, peripheral channel which collects the oil issuing from the perforated base of each of the rings when the press is working.

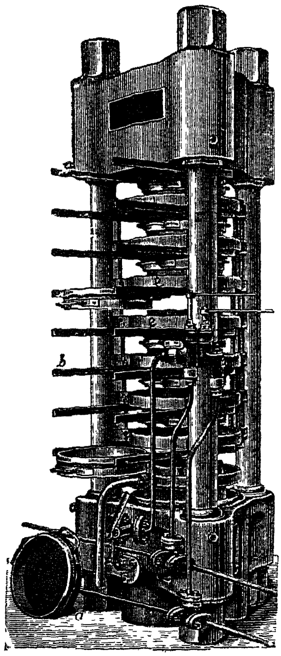


FIG. 261.

The automatic changing of the rings requires 1 to 2 minutes, about the same length of time being occupied in discharging them, while, under a pressure of 200 to 300 atmos., the pressing is complete in 8 to 10 minutes. Especially with palm oil and coco-nut oil, the pressing may be carried out in the hot, the plates being arranged so that they can be heated; this procedure shortens the time of pressing and increases the yield of oil. In some cases the pressing is carried out first at a low pressure, which gives an oil of improved quality, the cake thus obtained being ground (*e.g.* by an Excelsior mill, p. 168) and squeezed under a high pressure for the extraction of a further quantity of oil of lower grade.

Extraction of the oil by means of solvents (first attempted in England in 1856), from the crushed seeds or broken cake, is effected with carbon disulphide (*see* vol. i, p. 396)—which has considerable solvent action on fats, even in the cold, but also removes a certain amount of chlorophyll—or with light petroleum (benzine), which exerts its maximum solvent effect in the hot. The use of carbon tetra-

[1] The HYDRAULIC PRESS is based on Pascal's principle, according to which a pressure exerted on any point of a liquid mass is transmitted with the same intensity in all directions So that, if a pressure of 1 kilo. is exerted, by means of a piston 1 sq. cm. in area, on a liquid in one arm of a U-tube, the other branch of which is closed by a piston 16 sq. cm in area, this would require a pressure of 16 kilos to balance the first piston (Fig. 262), the pressure transmitted by the pressing surface being proportional to the area receiving the pressure.

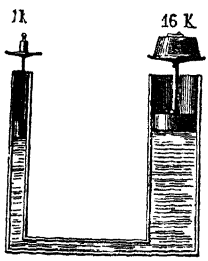


FIG. 262.

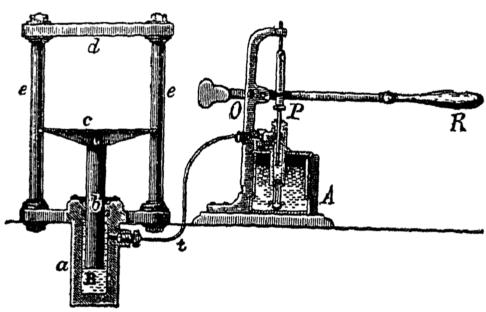


FIG. 263.

The hydraulic press consists of a suction pump, *P* (Fig. 263), which draws water from the reservoir, *A*, and forces it through the strong copper tube, *t*, into the thick-walled chamber, *B*, hermetically sealed at the upper part by a large piston, *b*, carrying a wide plate, *c*, on which is placed the material to be compressed. The compressing surface is that of the base of the small pump-piston and the surface receiving the pressure is given by the base of the piston, *b*, the pressure received being dependent on the ratio of the sections of the pistons and on the ratio between the arms, *OP* and *PR*, of the pump-lever. If *PR* is ten times as long as *PO* and the force exerted at *R* is 30 kilos, the piston of the pump receives a pressure of 300 kilos (30 × 10); if, on the other hand, the section of the large piston, *b*, is 15 times as great as that of the small piston, the pressure exerted on the latter will be 4500 kilos (300 × 15)

When the piston, *b*, rises, the plate presses the substance against a strong cover, *d*, fixed by three or four

chloride has also been suggested recently (*see* vol. i, p. 378), since it is not inflammable like the other two solvents and, further, allows of the extraction of the oil from moist substances.

The extraction can be carried out by direct exhaustion or by systematic exhaustion. In the former case, the substance is treated with pure solvent, so that large quantities of dilute solutions which must be concentrated are obtained; in the other process, a number of apparatus are arranged in a series so that the solvent passes from one to the other and leaves the last completely saturated, while the first apparatus, as it becomes exhausted, is charged with fresh material and placed last in the series (*see* vol. i, p. 470, and exhaustion of beet in the diffusers, under the heading Sugar, *later*). From the saturated solution of the oil, the solvent is distilled by means of direct or indirect steam and is thus completely recovered, while the crude fat remaining is refined.

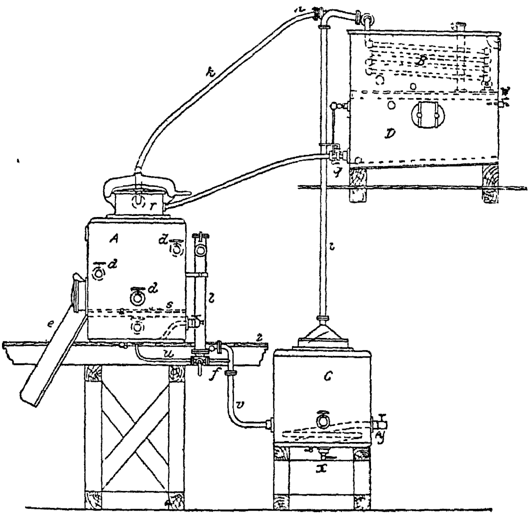


FIG. 264.

There are various forms of apparatus corresponding with the first method of extraction, such as the *Merz universal extractor*, that of Pallenberg, and the Wegelin and Hubner (Fig. 264) form, which is fairly widely used. In the last of these the fatty material is placed in the vessel, A, into which solvent is introduced from D by means of the tube, $r\,q$. The solvent saturated with fat is discharged into the still, C, where, by means of indirect steam passing through the coil, y, the solvent is distilled, its vapour ascending the tube, i, and condensing in B, and the liquid collecting in D. The fat remaining in

columns, *e*. When the pressure is to be released, the water is discharged from the chamber, B, and the piston descends. The pump is provided with a safety-valve which regulates the maximum pressure desired. The large piston is made tight by encircling it at b with a leather ring (devised by the Englishman Bramah) with an inverted U-section; the water, in its attempts to escape along the sides of the piston, enters the ring and forces its edges against the piston with a pressure increasing with the pressure of the water, and thus forms a true hermetic seal.

Nowadays horizontal hydraulic presses, which discharge the oil and cake more easily, are also used, but these occupy more space, while at the same time the piston does not recede of itself at the end of the operation.

In practice, when a substance is to be compressed with a hydraulic press, two or more pumps are used. The first, which has a long stroke, raises the piston and plate rapidly, since at first the resistance is small; when the pressure increases, the compression is continued more slowly by means of a small pump.

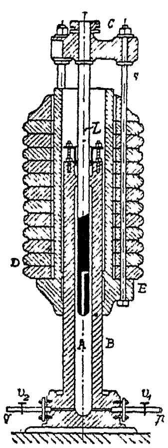


FIG. 265.

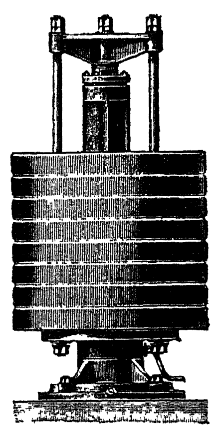


FIG. 266.

To avoid attention to a number of pumps and loss of energy, works employing many hydraulic presses make use of the so-called *hydraulic accumulators* (Armstrong, 1843), which provide a store of water under high pressure for the feeding of several presses at once (Figs 265 and 266). A piston, L, moving in a cylinder, B, just as in an ordinary hydraulic press, receives pressure from below by means of compressed water from a pump, passing through p and v_1; the upper part of the piston is fixed to the centre of a plate, C, which, by means of three columns, S, supports the plate, E, carrying the heavy iron discs, D. When the piston is raised by the compressed water entering A, the whole accumulator, E, C, and the discs, D, are raised. When v_1 is closed, A contains a store of water under great pressure which transmits pressure to a number of hydraulic presses simultaneously when the cock, v_2, communicating with these presses is opened. In order to prevent the piston, L, from being raised too much and so forced out of the cylinder, B, the lower part of the piston is provided with a small vertical channel with a lateral exit; when the latter is forced from the top of the cylinder, B, the water escapes, the pressure is lowered and the piston falls. Large works are supplied with two or more accumulators, so that when

C can then be drawn off through the tap, *x*, but if it retains solvent tenaciously, it is first heated by a current of direct steam, solvent and water then condensing together in the condenser, *B* ; owing to their mutual insolubility, these two liquids can be separated by means of a suitable separator situated at *w* between *B* and *D*, the water being thrown out. If the solvent saturated with fat, instead of being drawn off by the tube, *u*, is caused to rise to the top to the tube, *l*, whence it falls into the tube, *v*, the extraction is effected with continuous circulation of the solvent until the substance is exhausted. To expel and recover the solvent retained by the substance remaining in *A*, a current of direct steam is passed into the latter ; this carries off the vaporised solvent along the tube, *k*, through the valve, *n*, to the cooling coil, *B*, the condensed water and oil being passed through the separator, *w*, before the latter liquid is collected in *D*.

Large works, however, always use batteries of extraction apparatus arranged in series.

In a good extracting plant, the loss of solvent does not usually exceed 0·5 per cent. of the weight of oil extracted and is always less than 1 per cent.

REFINING of oils, to separate as far as possible the tannin, protein, and colouring-matters extracted from the oily seeds and fruits, is generally effected by means of dehydrating or oxidising agents (the latter attack the colouring-matters more especially).

In order that sulphuric acid may not act on the glycerides (forming ethers) and heat and partially carbonise the oil, it must be used at a concentration of about 60° Bé. and in small quantity (1 to 2 per cent.) with oil heated to 50° to 60°, or with the cold oil ; under these conditions the few impurities are first carbonised and the oil becomes coloured, but after filtration it is obtained paler, purer, and clear.

Zinc chloride often gives almost the same results as sulphuric acid, and is added in concentrated solution (sp. gr. 1·85) and in amounts up to 1·5 per cent. of the oil ; the black flocculent matter formed separates on standing or filtration.

In some cases it is sufficient to leave the oil in large closed tanks of tinned iron with conical bases fitted with taps so that the impurities which gradually settle may be removed. Fragments of coal, peat, willow, &c., may be added, these carrying down the impurities as they settle. In order to avoid prolonged contact of the oil with the air, pressure filters (described in the section on Sugar) are preferred ; either the oil is placed at a higher altitude than the filter, or the pressure is applied by means of pumps, it being possible in this way to filter 1000 to 2000 kilos of oil in 24 hours. To purify with sulphuric acid (*see later*, Twitchell process), the latter is poured in a thin stream into the oil contained in a lead-lined vat and kept well stirred. After 7 to 8 hours, by which time small black clots of carbonised impurities have deposited, the oil is decanted into a second vat, washed two or three times with water at 40° to 60° (in some cases a small quantity of sodium carbonate is added to the second water), being stirred meanwhile or emulsified by air from a Körting injector ; after being left to stand, it is either decanted or filtered.

The water is sometimes intimately mixed with the oil to be washed by means of the so-called *emulsor-centrifuge* (Fig. 267), consisting of two superposed metal plates with the concave parts inside and mounted on a hollow axle rotatable at 8000 to 10,000 revs. per minute, while through a central aperture commanded by two taps—exactly adjustable—the oil and water are introduced in the desired proportions. The distance between the two plates can be altered so as to give a slit between their edges from 0·02 to 2 mm. in width, the more or less completely emulsified mass being forced out through the slit by the plates themselves. If the oil does not separate from the water on standing, the emulsion may be destroyed by added powdered and calcined sodium sulphate or carbonate (which act as dehydrating agents) or by agitating the emulsion with animal black or

one is raised and the other at its low position, excess of compressed water supplied by the pumps at any moment is directed to the latter accumulator, which is hence raised. In this way, also, the final pressure of the hydraulic press can be utilised before discharging it, energy being thus saved that would otherwise be lost.

By these means, a uniform and persistent pressure may be exerted on several presses, but it is exerted, not gradually, but instantaneously, which may be disadvantageous in certain cases, unless indeed various accumulators at different pressures are employed. Accumulators with small pistons may be used for pressures up to 400 atmos. The circular iron rings composing the accumulator may be replaced by a single large cylinder filled with scrap iron or stones.

The pressure of a hydraulic accumulator may be exerted in some degree gradually by connecting it with a compressed-air chamber (*automatic accumulator*). As liquid for use in the accumulators, water, glycerine, or oil may be employed.

magnesium silicate (which separates the components); but the best results are obtained with *centrifugal separators*, like that used for milk (see p. 387), the water and impurities being forced to the periphery, where they adhere, while the oil is discharged by the central tube. The acid may also be mixed in the same way and continuous working may be attained by means of a battery of emulsors and another of centrifugal separators; the latter serve well to purify the dregs of the oil and, in general, colloidal and soapy products of oils. When the emulsified or colloidal condition is due to the presence of gum or wax, it is preferable to initiate freezing of the glycerides, this breaking down the emulsion so that it can be filtered. When *stable emulsions* of oil and water are required, as is sometimes the case, they can be obtained by pouring the oil into a mixture of water and the amide of a higher fatty acid or an acidyl derivative of an aromatic base, or both of these, together with the salt of a higher fatty acid (Kösters, 1906).

To *deodorise* oils, they are passed through bone-black or, sometimes, elm-bark. In some cases, and more especially when very rancid, oils are purified by *deacidifying* them with a concentrated solution (8° to 10° Bé. for cotton-seed oil and 36° to 38° Bé. for olive oil) of caustic soda in amount slightly exceeding that calculated from the acid number; this treatment, however, readily leads to the formation of persistent emulsions and to loss of glycerides and also of fatty acids. These emulsions, which are due to the presence of soaps, are broken down in the manner already described, first being heated to 50° to 60°. If the acidity exceeds 30 per cent., the losses would be so high that deacidification is not advisable; such oils (*e.g.* highly acid olive oil after refining with sulphuric acid) cannot be used as lubricants or for softening wool, but are used solely for soap, unless indeed the fatty acids are transformed into glycerides by treatment with glycerine as described on p. 373.

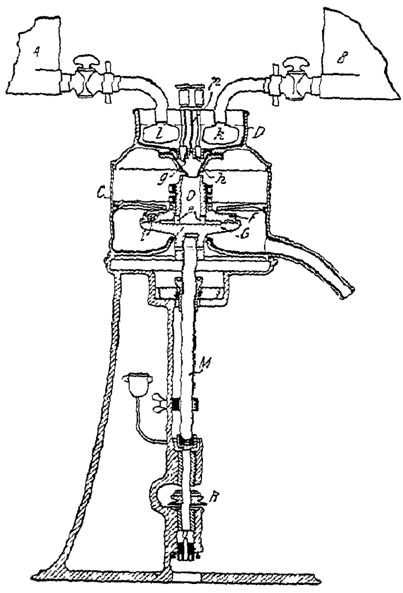


FIG. 267.

Bleaching with hydrogen peroxide, dichromate or permanganate is carried out as with tallow (see p. 381), but if the oil is first deacidified, 100 grms. (instead of 1500 grms.) of dichromate per quintal are sufficient. If it is required to eliminate every trace of soap, the oil is heated with a boiling solution of 5 per cent. sulphuric acid. Vegetable oils are frequently decolorised nowadays with fuller's-earth (see p. 77).[1]

OLIVE OIL is obtained by pressing the fresh olives of *Olea europœa* in the period from October to December (in Morocco, in August and September). The olive grows in abundance in Central and Southern Italy, on the shores of Lake Garda, on the Genoese Riviera, and in Southern France, Spain, Portugal, Dalmatia, Istria, Greece, Morocco, California, and Southern India.

The composition of the fruit is given in the Table on p. 391.

It is not advisable to extract the oil from stored or fermented olives, these giving the so-called *huile tournante*, which is rich in fatty acids and yields a persistent emulsion when shaken with soda solution, and a *Turkey-red oil*—similar to the sulphoricinate (see p. 327)—when treated with concentrated sulphuric acid.

If the olives cannot be worked at once, fermentation is prevented by storing them in a cold, dry, and well-ventilated place. The fermentation (according to Tolomei) is due to an enzyme (*olease*) occurring with the oil, which, in the presence of air and light, it

[1] Fuller's-earth has been long used in Northern Africa for clarifying olive oil; in Chicago it was thus employed as early as 1878, but its use was considerably extended subsequently to 1890. It consists of aluminium and magnesium hydrosilicates, and is found in granular or powdery deposits in Florida and also at Fraustadt, in Silesia. The decolorising action of this earth depends on its state of hydration, the maximum effect being obtained if it is first lightly roasted (at about 200°), while if the roasting is carried too far so that all the water of hydration is lost, the decolorising power is entirely destroyed. The oil is shaken with 1 to 3 per cent of the earth, and the mass heated for a short time at a temperature (60° to 100°) varying with the nature of the oil and then passed to the filter-press, the first turbid portions of the filtrate being refiltered.

decolorises; if the olease is removed by washing the oil with water, the oil is not decolorised under the influence of light.

The extraction of olive oil is not always effected by rational processes and plant, but usually the olives are first crushed by means of the ordinary edge-runners (*see* Fig. 210, p. 251).

The pulp is next placed in suitable bags of tenacious vegetable fibre or wool surrounded by horsehair and then pressed, the type of press employed varying widely with the locality. The ring hydraulic press (*see* Fig. 261, p. 392) and other forms, still further improved, give excellent results. In some cases a moderate pressure is first employed, the result being oil of superfine quality (*virgin oil*). The residues are steeped in hot water and subjected to increased pressure. Repetition of this procedure, employing a still higher pressure, gives an industrial oil. The cake from the second pressing may, however, be agitated in a vat through which water flows; part of the remaining oil is thus removed, this being collected in a second vat, where it undergoes protracted washing with water, yielding so-called *washed oil.*

The Kuess-Funaro process (1902), which results in an improved yield and a readier extraction, consists in emulsifying each time with feebly alkaline aqueous solutions.[1]

The residual cakes (known in Italy as *sanse*), after being dried, still contain 7 to 11 per cent. of oil, which is nowadays extracted in large works by means of carbon disulphide, which gives the very green, so-called *sulphocarbon oil,* almost all of this being used in the manufacture of green soap for the textile industries.[2]

Pure olive oil is yellowish or, in some cases, almost colourless or slightly green. The finer qualities taste but little; freshly pressed Puglia oil has a rather bitter and unpleasant taste (due to camphene, eugenol, and other substances investigated by Canzoneri), which it gradually loses.

The *composition* of olive oil varies with the district of origin and with the conditions of extraction, the solid glycerides fluctuating from 10 to 28 per cent. (more especially palmitin). The liquid glycerides, which occur to the extent of 70 to 90 per cent., were formerly thought to consist of triolein alone, but the presence of linoleic acid (as much as 6 per cent., this explaining the high iodine number of the oil) has now been proved, and there appears also to be about 1·5 per cent. of a mixed glyceride and 0·2 to 1·5 per cent. of volatile acids, besides 0·7 to 1·6 per cent. of non-saponifiable substances (phytosterol and, according to Sani, an oil not yet defined). It contains a variable quantity of free fatty acids, and when impure readily becomes rancid. If the acid number exceeds 16 (*i.e.* 8·1 per cent. of acids calculated as oleic acid), it cannot be used as machine oil as it attacks metals.

[1] A new process of extracting olive oil proposed by Acapulco (1910–1911) and tested with favourable results in the experimental oil plant of the Portici Higher Agricultural School, is based on the different surface tensions of the two liquids (oil and water) which are present in the pulp of the olive and have to be separated, and hence on their different capillary behaviour towards the vegetable tissues constituting the pulp The surface tension of the oil is about one-half of that of the water, so that separation of the two liquids is easily attained by even slight diminution of the pressure below that of the atmosphere. The separation is also facilitated by rise of temperature and by the fact that the water present has a capillary constant higher than that of the oil, so that it remains more strongly adherent to the vegetable tissues The essential part of the machinery of this process —after the stones have been separated from the pulp—consists of the so-called filtering extractors, formed of superposed metallic cylinders, inside which is a metal filtering cloth, an annular space communicating with the vacuum pump being left between the walls and the cloth. A stirrer fitted with vanes continually moves the mass of pulp contained in the extractor and spreads it in thin layers on the filtering cloth so that the liquid portion is separated from the pulp. By steam-heating the extraction can be carried out at any temperature. But even in the cold the exhaustion of the pulp is more complete than that obtained by the older systems, while in the hot it surpasses that reached by pressing the "sanse" in the most powerful hydraulic presses. It is said that the Acapulco process is more economical than those previously used and that it lends itself to the production on a large scale of pure, slightly coloured oils of constant type. But, as yet, this process has not been subjected to decisive commercial tests.

[2] To distinguish *sulphocarbon oil*, which has a lower iodine number (77 to 80), from that obtained by pressure, Halphen's test (1905) may be employed. To 50 c.c. of the oil heated to 100° are added 12 c.c. of alcoholic caustic potash diluted with an equal volume of water, the mixture being heated for ten minutes at 110° and cooled to 100°; 200 c c. of hot water are then added and the liquid, after cooling, shaken with 200 c.c. of saturated sodium sulphate solution; 20 c.c. of 30 per cent. copper sulphate are then added, and the liquid filtered. If the filtrate is not green, a little more of the copper sulphate solution is added and the liquid filtered again if necessary. 5 c.c. of silver nitrate solution (containing 1 vol. of 1 per cent. aqueous silver nitrate solution and 5 vols. of glacial acetic acid) are then added to the liquid, which is boiled, allowed to cool, supersaturated with ammonia and filtered, the filter being washed with dilute ammonia. If black silver sulphide remains on the filter, the presence of sulpho-carbon oil (or *impure* cruciferous oils—colza, mustard, &c.—which cannot be detected otherwise) is certain. Cusson (1909) has devised a simpler test: 200 grms. of the oil are vigorously shaken with 50 grms. of 90 per cent. alcohol and then distilled on a water-bath, the distillate being collected in a well-cooled flask containing a little alcoholic potash Even traces of carbon disulphide thus yield potassium xanthate, which gives a yellow coloration or precipitate on addition of *alcoholic cupric* acetate solution.

Pure olive oil is used as a comestible and the very pure and more liquid qualities for oiling clocks, while the other qualities are employed in large quantities in the manufacture of soap, lubricants, burning oil, and Turkey-red oil.

The purity of the oil is controlled by various tests referring to the constants given in the Table on p. 378, and by certain special tests. Olive oils of certain origins give abnormal constants, *e.g.* Algerian and Moroccan oils have an iodine number of 96 and are reddened by nitric acid ; pure Tunisian olive oil gives the reaction for sesamé oil (Villavecchia and Fabris' test) but not the Belliez reaction (test for sesamé oil with a saturated solution of resorcinol in benzene and nitric acid) ; the extraneous substances of Tunisian oil which give the Villavecchia and Fabris test can be removed by shaking the oil with hot water. Detection of added *sesamé oil* is effected by Tortelli and Ruggeri's modification of Baudouin's test on the fatty acids (*see* p. 384), or more rapidly on the oil itself by means of Villavecchia and Fabris' test, taking care to dilute 5 c.c. of the resulting red acid liquid with four times its volume of distilled water and to shake the mixture in a cylinder, and observing the lapse of time required for the disappearance of the red coloration. With *any* pure olive oil, if there is a coloration, this disappears within 5 minutes or, in exceptional cases, in 8 minutes, whilst if sesamé oil (even only 3 per cent.) is present the colour will persist for 30 minutes (Zega and Todorovic, 1909). The presence of *cotton-seed oil* is indicated by the Halphen reaction (*see* p. 381) or by Tortelli and Ruggeri's modification of Becchi's reaction, which is carried out on the liquid fatty acids in the following manner : 20 c.c. of the suspected oil are hydrolysed with alcoholic potash in the ordinary way (*see* p. 379), the aqueous solution of the soap being neutralised with acetic acid and precipitated with lead acetate ; the lead salt, separated by filtration, is shaken with ether and the filtered ethereal solution decomposed in a separating funnel by dilute hydrochloric acid. The ethereal layer is filtered and the ether evaporated, and to 5 c.c. of the residue (liquid fatty acids) [1] are added 10 c.c. of 90 per cent. alcohol and 1 c.c. of 5 per cent. aqueous silver nitrate solution ; if a black precipitate is then formed on heating for some time on a water-bath at 60° to 70°, the presence of cotton-seed oil is proved. In certain special cases the Becchi reaction alone is insufficient to indicate with certainty the presence of cotton-seed oil. Traces of *mineral oils* in vegetable oils are detected by the formation of a yellowish red solution on addition of a benzene solution of commercial picric acid (F. Schulz, 1908; *see* Note, p. 379). To detect *fish oil* in vegetable oil, 100 drops of the latter are treated with a mixture of 3 c.c. of chloroform and 3 c.c. of acetic acid, sufficient bromine being then added to produce a persistent brown coloration ; after ten minutes rest the vessel is introduced into boiling water, when the liquid will remain liquid if the vegetable oil is pure, whilst insoluble bromo-compounds will separate if fish oil is present. With boiled oil, the metals are first eliminated. Where the oil has been coloured yellow with *auramine*, this is detected by boiling 1 c.c. of the oil with 20 c.c. of 8 per cent. alcoholic potash and a little zinc powder in a reflux apparatus, 20 c.c. of pure benzene and 50 c.c. of water being added after cooling ; the benzene solution is evaporated and the residue taken up in glacial acetic acid, a blue coloration, becoming darker on heating, being formed if auramine is present. *Sanse oil* or sulphocarbon oil, extracted from the cake or *marc* by means of carbon disulphide, has a dark green colour, and the corresponding fatty acids have a rather low iodine number (as low as 75) and a somewhat higher melting-point than usual.

The presence of *arachis oil* in olive oil is shown by the Tortelli and Ruggeri test, which has been modified by Fachini and Dorta (1910) as follows : 20 grms. of the oil are saponified with alcoholic potash, the alcohol being then expelled, the soap dissolved in water, the fatty acids liberated by hot dilute sulphuric acid, and the clear fused acids collected on a moist filter ; they are then washed with hot water and dissolved in 150 c.c. of pure, tepid acetone, water being subsequently added, drop by drop, until a turbidity is formed ; the liquid is finally rendered clear by the addition of a few drops of acetone at 40° to 45° and then left to crystallise. In presence of arachis oil, characteristic shining crystals separate at 15° ; after an hour these are collected on a filter, washed with 10 c.c. of dilute acetone (32 vols. water + 68 vols. acetone) and examined for arachic and lignoceric acids by the Tortelli

[1] The *liquid fatty acids* can be separated, to a considerable extent if not quantitatively, from the solid ones by dissolving the mixtures in light petroleum or, better, in acetone and crystallising out almost all the solid fatty acids by cooling (to −20°) (Fachini and Dorta, 1910). According to Twitchell (U.S. Pat. 918,612, 1909) the liquid fatty acids are separated from the solid ones by fusion with 1 per cent. of aliphatic sulpho-acids, which render the liquid acids soluble even in water.

and Ruggeri test: one-half is dissolved in 100 c.c. of 70 per cent. alcohol, warmed slightly and allowed to cool, separation of crystals indicating arachidic acid (m.pt. 75° to 76°) with certainty.

STATISTICS.—The cultivation of the olive is widespread in Italy, where it extends to over a million hectares. The production and price vary considerably from year to year, sometimes causing serious agricultural crises. The production of the oil varies from 2 to 4 millions of hectolitres (250,000 to 350,000 being sulphocarbon oil). The mean annual production per hectare was 3·66 hectols. in 1879 (total, 3,400,000 hectols.) and 2·5 hectols. in 1899, the total being 2,515,000 hectols. The total production in Italy was 3,086,000 hectols. (3·04 per hectare) in 1890; 2,337,000 (2·16) in 1901; 1,846,000 (1·7) in 1902; 3,256,000 (2·99) in 1903; 3,412,300 in 1906; 2,559,000 (corresponding with 15,000,000 quintals of olives) in 1909; 1,384,580 (9,366,000 quintals of olives) in 1910.

The *exportation* from Italy was 412,000 hectols. in 1898; 506,000 in 1899; 290,000 in 1900; 424,350 in 1901—120,000–140,000 to France, 100,000 to Russia, 50,000 to North and 55,000–80,000 to South America, 60,000–80,000 to England, and 42,000–52,000 to Austria-Hungary. In 1908 the exports were 368,000 quintals (91,800 to the United States and 127,000 to the Argentine); in 1909, 184,500; and in 1910, 285,150 (96,000 to the United States, 73,500 to the Argentine, and 40,000 to France). The price varies according to the harvest in the different districts and to the requirements abroad; in some years the producers sell at £4 per hectolitre and in others at 48*s*. to 56*s*. In 1908–1909, owing to the small crop in Puglio, caused largely by the drought, prices exceeded £7 10*s*. per quintal. In 1907 the products of the olive industry of Italy alone were valued at more than £8,000,000 (oil and residues); the number of presses was 52,000, these being distributed in 18,000 works, of which only 2400 employed steam. During the two or three months of the olive campaign, about 70,000 operatives are employed. Extraction of the oil by means of carbon disulphide is carried out in 60 works, consuming 780 h.p. (almost all steam-power) and employing 1230 workmen. The exportation of sulphocarbon and washed oil was about 60,000 quintals in 1900, 100,000 in 1904, 55,660 in 1909, and 131,400 in 1910. Italy imports olive oil every year, especially from Spain and Greece, the total amount being 39,000 quintals in 1908, 52,330 in 1909, and 58,450 in 1910. Portugal produces 250,000 to 350,000 hectols. per annum, and Spain (especially in Andalusia) about 2 or 3 millions of hectols., of lower quality than the Italian. In 1905 the Spanish production was 1,492,490 quintals, and in 1906, 1,336,650; the amount exported being 340,000 quintals in 1905, 190,000 in 1906, and about 150,000 in 1907.

France, with about 150,000 hectares under olives, produces annually about 1,500,000 hectols. of oil. Greece produces 550,000 hectols. (in 1907); Asiatic Turkey (with Crete), 2,000,000 hectols., importing also 350,000–500,000 hectols., especially from Spain, Italy, Tunis, and Algeria, and exporting 200,000–250,000 hectols. of the finest quality. In 1906 Tunis produced 243,000 hectols., and in 1907 almost 400,000.

The *world's production* is about 10,000,000 hectols. of the oil. Germany imports 10,000–13,000 tons, seven-tenths of it for industrial purposes. Austria imports about 6000 tons. England imported crude olive oil to the value of £300,000 and purified oil to the value of £386,190 in 1910. The imports into the United States were valued at £1,162,400 in 1910 and at £1,149,800 in 1911.

CASTOR OIL is extracted from the seeds of *Ricinus communis*, a plant cultivated in India, Italy, Messina, California, Egypt, and Greece. The oval seeds are 10 to 15 mm. long, about 6 mm. broad, and rather flat, and are covered with a brownish or marbled, shining, brittle skin; when peeled they contain 45 to 55 per cent. of oil.

The oil was at one time extracted by pressing the ground seeds twice in the dry state and then pressing the residue after steeping in hot water. Nowadays, however, three consecutive pressings of the hot crushed seeds with increasing pressures are employed, modern hydraulic presses being used. This procedure yields first a fairly pure pale oil, then one less pure, and finally a more highly coloured oil for secondary industrial purposes. One hundred kilos of the seeds yield 9 kilos of husks, 43 of residual cake, 20 of oil of the first, 10 of the second, and 8 of the third pressing. The oil is purified by heating with an equal volume of boiling water, which precipitates many protein and gummy substances; it is decolorised by means of bone-black or by the ordinary processes given for tallow.

The refined oil is almost colourless or faintly yellow, and has a high specific gravity,

considerable viscosity, and a peculiar, unpleasant taste and smell. It forms an excellent purgative, the less pure qualities being used in the manufacture of *sulphoricinate* (*see* p. 327) and of transparent soaps capable of retaining considerable quantities of water. Its soap differs from others in not rendering water opalescent. The residual cake, whether extracted with carbon disulphide or not, is injurious and cannot be used as cattle-food, but it is of value as manure, since it contains 4 to 5 per cent. of combined nitrogen and is sold at 8*s*. to 10*s*. per quintal.

Castor oil contains various glycerides but is free from tripalmitin. Triricinolein is solid, and there appear to be glycerides of a *ricinoleic acid* and of a *ricinisoleic acid*, also of a hydroxystearic acid (melting at 141° to 143°) and a dihydroxystearic acid (which explains the characteristic high acetyl number of castor oil).

The oil yields, besides ricinoleic acid, more or less highly polymerised compounds with less and less marked acid characters (*e.g.* ricinisoleic acid), these increasing in amount with the age of the oil.

Castor oil is strongly dextro-rotatory (40·7° in a 20 mm. tube). Unlike other oils, it is soluble in all proportions in absolute alcohol and in glacial acetic acid ; at 15° it dissolves in 2 parts of 90 per cent. alcohol or 4 parts of 84 per cent. alcohol, but is insoluble in light petroleum or paraffin oil (both of which dissolve all other oils and fats). Hence, if a castor oil is insoluble in light petroleum and gives a clear solution with 5 vols. of 90 per cent. alcohol, it may be regarded as pure. The solubility relations are completely inverted if it is heated to 300° and 10 to 12 per cent. of it distilled ; there then remains a product termed *floricin*, which solidifies at –20°, is insoluble in alcohol, dissolves in all proportions in mineral oil, and forms a stable emulsion with 5 parts of water. A similar product is also obtained by heating castor oil to 200° in presence of 1 per cent. of formaldehyde ; if heated with zinc chloride solution, it becomes dense. The potassium salt of the condensed product, with water and formaldehyde, gives a disinfectant solution producing the same effects as lysoform or ozoform.

The constants of castor oil are given in the Table on p. 378.

Italy produces a certain quantity of castor oil seeds, but the greater part is imported, this amounting to about 55,000 quintals in 1892 and 80,000 (equal to about 27,000 quintals of oil) in 1904. In 1901 Italy exported 5420 quintals of castor oil ; in 1908, 3454 ; in 1909, 2292 ; and in 1910, 4766 quintals of the value of £18,110. In 1908 Germany imported 62,400 quintals of castor oil, and in 1909, 85,000.

LINSEED OIL is a drying oil, as it contains much linoleic and linolenic acids (*see* pp. 303 and 304), and when spread out in a thin layer on a sheet of glass slowly forms a solid skin (varnish), this forming more rapidly with the boiled oil.

Linseed oil is extracted from the seeds (containing 35 per cent. of oil) of *Linum usitatissimum*, which are converted into flour by the ordinary edge-runner mills and pressed hot in hydraulic presses.

Linseed is cultivated especially in the Baltic provinces of Russia, and also in Southern Russia, Eastern India, the United States, and the Argentine, and to a less extent in Egypt, Belgium, and Italy. Linseed oil extracted by means of solvents contains more unsaturated fatty acids and less volatile acids than the expressed oil.

According to Fahrion (1903 and 1910), the fatty acids separated from linseed oil contain 17·5 per cent. of oleic acid, 30 per cent. of linolic acid, 38 per cent. of linolenic and isolinolenic acids, 8 per cent. of palmitic and stearic acids, all combined with 4·2 per cent. of glycerine and 0·6 per cent. of non-saponifiable substances.

The purity of the oil is indicated by means of the constants given in the Table on p. 378, especially by the iodine number and the refractive index, which, in the different qualities, varies from 1·484 to 1·488 at 15° (or from 81 to 85 Zeiss at 25° or 87 to 91 Zeiss at 15°), whilst cotton-seed oil gives no more than 1·477 and maize oil no more than 1·4765 at 15°.

A good proportion of the oil is used in practice in the form of *boiled linseed oil* (*see* Note on next page), since on boiling it acquires drying properties especially necessary to the varnishes prepared with the oil.

The *drying power* can be determined by Livache's method. On a watch-glass is spread 1 grm. of lead-powder (obtained by immersing a strip of zinc in the solution of a lead salt and washing the precipitate with water, alcohol and ether, and drying), on which 0·6 to 0·7 grm. of oil is allowed to fall slowly in drops, the whole being then weighed exactly and left at a moderate temperature in a well-lighted situation. After 18 hours the weight

begins to increase, the maximum increase (12 to 15 per cent.) being obtained within 2 or at most 3 days (it then diminishes slightly). Other drying oils give the following increases: *walnut oil*, 7·9 per cent.; *poppy-seed oil*, 6·8 per cent.; *cotton-seed oil*, 5·9 per cent.; *cod-liver oil*, 7·4 per cent.; the remaining oils increase in weight only after the fourth or fifth day to a maximum of 2·9 per cent. after seven days. The *drying properties* are determined best and most rapidly by spreading a given weight of the boiled linseed oil on a definite area of glass (1 mgrm. per sq. cm.) and leaving the latter in a horizontal position until the oil is no longer adhesive when pressed lightly with the finger (the temperature should always be noted). The drying power of an oil can be determined also from the ozone number (Molinari and Scansetti, 1910).

In a 20 mm. tube, pure linseed oil gives a rotation of $-0·3°$ in the Laurent saccharimeter at 15°, whilst other resin oils and sesamé oil are dextro-rotatory.

Linseed oil is used mostly in the manufacture of *lacs* and *varnishes*,[1] mastics and *linoleum*. The latter is obtained by oxidising (blowing) hot linseed oil, after addition of the dryer (*see* Note), for 18 to 20 hours with hot air until it thickens to linoxyn; about 30 per cent. of colophony are then added, the whole being converted into a paste with cork-dust at a temperature exceeding 100°. The mass swells and is compressed hot (140°) on a strong textile previously varnished to protect it from moisture, the whole being repeatedly pressed between hot rollers. It is finally dried in suitable hot chambers, where it loses its smell and acquires elasticity and weight. It is coloured in the pasty condition with mineral colouring-matters.

Linseed oil is used also for making soft, transparent soaps (*see* later).

STATISTICS. Almost the whole of the linseed oil produced comes from India, Russia (about one-fourth), North America, and the Argentine. From 1895 to 1900 it amounted to about 1,500,000 tons, while in 1903 it exceeded 2,500,000 tons, the price varying from £10 to £12 per ton. North America produces about 200,000 tons of the oil; the exports include very little oil but comprise 500,000 tons of cake out of a total of 700,000 produced. The imports of linseed oil to the United States were valued at £72,600 in 1911 and the

[1] **Oil Varnishes and Lacs** are liquids which, when spread out in a thin layer on an object, leave on drying a solid, shining skin insoluble in ether and water and almost impermeable. Varnishes and lacs have linseed oil as a basis, and are often mixed with mineral or organic colouring-matters. Oil varnishes are formed from linseed oil rendered drying by dissolving small quantities of certain minerals in the hot. Oil lacs are obtained by adding to the almost boiling oil varnish (free from gummy matter) the fused copal or other resin, and diluting with oil of turpentine at the moment of using: all these new components contribute to increase the fixation of oxygen. Crude linseed oil requires four to five days to dry in a thin layer, but the fixing of oxygen, that is, the drying, may be markedly accelerated by the presence of small quantities of dissolved metals which act as catalysts.

At one time oil varnish (boiled linseed oil) was prepared by heating the oil to 220° to 300° for 2 to 3 hours in presence of minium, litharge, or manganese dioxide (*dryers*). This procedure yielded dark varnishes (*boiled varnishes*), and was accompanied by danger from fire, the heating being carried out in open iron vessels furnished with stirrers and heated directly over the fire. Nowadays the dryer (0·1 to 0·25 per cent. Mn or 0·5 per cent. Pb + 0·1 per cent. Mn is sufficient) is dissolved by heating at a far lower temperature (100° to 120° and best in a vacuum) for 4 or 5 hours (by indirect steam at 135° to 150°), it being added (when the oil ceases frothing) as manganese borate or, better, manganese linoleate or resinate, and the mass stirred with compressed air; in this way, the so-called *cold varnishes* are obtained. These are paler varnishes which dry in 6 to 8 hours, whilst the others require as long as 24 hours. It has been proposed to decolorise boiled linseed oil with ultra-violet rays. The *drying* is far more rapid in the hot than in the cold. Prolonged boiling of linseed oil without dryers increases not so much the drying properties as the consistency, certain components of the oil being polymerised and the iodine number consequently diminished; these oils, thickened at 295° to 340°, bear the names *Dickol*, *Standol*, and *lithographers' varnish*. The action of oxygen during the drying of varnishes seems to lead to the decomposition of the glycerides of the saturated acids and of oleic acid with subsequent complete oxidation of the glycerine and acids, the glyceride of hydroxylinolic acid (*hydroxylinolein*), insoluble in ether, being also formed as well as anhydrides and polymerised substances.

In the manufacture of *lacs*, a difficult and important operation is the fusion of the copal—previously prepared in lumps—in cylindrical or slightly conical, enamelled iron or aluminium vessels; these are protected at the bottom by an iron or copper casing when heated by direct-fire heat and are provided with a cover and chimney to carry off the noxious vapours, which are carefully condensed or burnt. The temperature is closely watched by means of a thermometer immersed in the fused copal (300° to 360°). It is nowadays regarded as preferable to heat with hot water under pressure (up to 300°) circulating in coils situate in the lower part of the boiler. Complete, uniform fusion occupies 3 to 4 hours (with a loss in weight of 15 to 30 per cent.), the linseed oil containing the dryer and heated to about 100° being then mixed in; if any turbidity appears, the mass is heated to 300°. It is then allowed to cool to 150° to 200°, the addition of the oil of turpentine—which dissolves the lac—and, if necessary, of the dryer, being then begun. The diluted lac is filtered under pressure and discharged into smaller vessels, in which it is allowed to cool completely. The addition of calcium salts of colophony renders the lac harder but more brittle.

The copal is sometimes replaced by colophony and other resins, which are, however, readily saponifiable; a mixture of Japanese wood oil with resin and a little lime gives a good lac. Lacs are improved by prolonged storage (at least a year). Linseed oil for making lacs should be free from gummy matters, which may be removed by filtration through magnesium aluminium hydrosilicate (*see* p. 395). The softer lacs contain more than 50 per cent. and the harder ones less than 50 per cent. of linseed oil.

The United States imported 12,000 tons (£488,000) of copal (kauri and dammar) in 1910 and 11,000 tons (£410,000) in 1911.

exports at £37,200 ; walnut oil to the value of £239,200 was also imported in 1911. Germany treated 142,000 tons of linseed in 1891, about 250,000 in 1900, and more than 331,000 in 1903 ; consequently the importation of linseed oil, which amounted to 35,700 tons in 1890, fell to 3350 tons in 1905 and to 2059 in 1909. The importation of oil-cake (mostly linseed) into Germany is, roughly, about 500,000 tons (exports, 180,000 tons). France imports about 150,000 tons of linseed (1905–1906). Holland imports more than 200,000 tons of linseed and exports 82,000 ; it imports also about 200,000 tons of linseed cake and exports about 25,000 tons of oil. England imported about 310,000 tons of linseed in 1900 and almost 506,000 tons in 1904 ; the imports of pure linseed oil amounted to 19,936 tons in 1909 and to 37,242 tons (£1,252,140) in 1910 ; 30,000 tons of the oil were exported in 1905, while in 1911 the exports were valued at £837,712. In 1905 Italy imported 1800 quintals of boiled linseed oil, and 3011 quintals (worth £9030) in 1910, besides 438,600 quintals of linseed in 1908 and 367,660 (worth £544,000) in 1910 ; the import duty is the same as for other vegetable oils, namely, 20*s*. 10*d*. (26 lire) per quintal for the boiled oil and 19*s*. 2*d*. (24 lire) for the crude. Italy also imported 26,432 quintals of varnish free from spirit, worth £150,920, in 1910.

PALM OIL is extracted from the fruit of certain varieties of palm (*Elais guineensis* and *Elais melanococca,* which grow in Western and Central Africa and in America, and *Astrocaryum acuale* and *Astrocaryum vulgare,* growing in Guiana). The orange-brown fruit, of the size of walnuts, hangs in bunches. The pulp constitutes, according to the variety, 25 to 75 per cent. of the fruit, which contains a nut also yielding an oil (*palm-nut* or *palm-kernel oil*).

The extraction of the oil in the districts where the palm is grown is carried out in an irrational manner, the fruit being sometimes heaped up until it putrefies and the oil then pressed out. In other cases the fruit is stored and compressed in excavations in clay soil, being left to putrefy until the oil separates at the surface. In other places the fruit is fermented for a month and then heated with water, so that the pulp becomes detached from the stone and can then be heated and pressed again with water until the fused oil comes to the top and can be decanted off. In these ways more than one-half of the oil is lost, and machinery is now being introduced for detaching and disintegrating the pulp and for the rational pressing of the latter.

When freshly expressed it has a buttery consistency, an intense orange-yellow colour and a faint smell of violets ; the colour and odour persist in the soap prepared from it. It can be decolorised by heating it when exposed to the air and light, but this is effected best and most rapidly by fusing and heating it until it loses the water remaining from any preliminary heating with water for the removal of impurities ; this separates from the fused mass in 24 hours. After this it is introduced into a metal vat or cylinder provided with a cover and tube for carrying the gases to the chimney ; the fat is heated to 100° by means of an indirect steam coil and a vigorous and finely divided stream of air passed through the oil from a perforated tube. In a couple of hours' time decolorisation is complete ; at the same time the pleasant odour of the fat remains, although it is destroyed if the fat is decolorised by simple heating to 220°.

Chemical decolorisation is often employed, the oil (1000 kilos), already purified by treatment with water and by fusion, being heated in a boiler to 50°, at which temperature 30 to 50 kilos of commercial hydrochloric acid and 8 to 10 kilos of potassium dichromate dissolved in 18 to 20 litres of boiling water are stirred in. After 15 to 20 minutes, 1 to 2 kilos of sulphuric acid are sometimes added, the stirring being continued until the oil becomes limpid ; stirring is then stopped and 70 to 80 kilos of boiling water sprayed on the oil to wash it. After standing overnight, the water is decanted off, the acid separated from below, and the oil washed once or twice by boiling with water.

Even when fresh it contains 12 per cent. of free fatty acids, and as it becomes older it decomposes spontaneously with increasing ease, separation of fatty acids (up to 55 per cent.) and glycerine—which can be extracted with water—taking place. Besides free palmitic acid, the principal components are the glycerides of oleic and palmitic acids, up to 1 per cent. of stearic acid, a little linolic acid, and about 1 per cent. of heptadecylic acid, $C_{17}H_{34}O_2$.

The colouring-matter of palm oil admits of various characteristic colour reactions : with sulphuric acid, a bluish green coloration is obtained, whilst mercurous nitrate colours it first canary-yellow, then pale green, and finally straw-yellow.

Palm oil is used in large quantities in the manufacture of soap and candles, its value being related to the melting-point of its fatty acids. It is calculated that the palm oil placed on the market (that is, exclusive of the large amounts consumed where produced) amounts to 70,000 to 80,000 tons per annum. Germany imports about 14,000 tons of palm oil and exports 14,000 to 18,000 tons of palm-nut oil and coco-nut oil. Marseilles imports 18,000 to 20,000 tons of palm oil and Austria-Hungary 3000 to 5000. England imported 176,264 tons of crude palm oil in 1909 and 199,438 tons (£3,056,600) in 1910, while the United States imported 42,000 tons in 1910 and 21,000 tons (£645,000) in 1911, in addition to 5000 tons of palm-kernel oil. The price varies with the year from 40*s*. to 52*s*. per quintal. The best qualities of palm oil are from Lagos; then come those of Old Calabar, Benin, and Accra; while among the more impure varieties are those from Gabun, Liberia, and the Cameroons.

PALM-NUT OIL (or **Palm-kernel Oil**) is obtained by crushing and then either pressing in hydraulic presses or extracting with solvents the stones contained in palm fruit; freed from shell, the seed forms 9 to 25 per cent. of the weight of the fruit and contains 43 to 55 per cent. of fat, which is white or straw-coloured and free from fatty acids when fresh, although it turns rancid fairly easily in the air; it melts at 26° to 30°.

It consists of about 15 to 25 per cent. of triolein, 33 per cent. of triglycerides of stearic, palmitic, and myristic acids, and about 45 to 55 per cent. of triglycerides of lauric (in preponderance), capric, caprylic, and caproic acids.

It bears a great resemblance to coco-nut oil, even in the property of its soaps of taking up large proportions of water—as much as 600 per cent. (coco-nut soap up to 1200 per cent.)—and of being somewhat soluble in solutions of salt. The total quantity of palm nuts placed on the market is about 1,125,000 tons. Germany now imports about 200,000 tons of palm nuts and copra (*see* Coco-nut), and 152,350 quintals of palm oil (in 1909); Austria, 30,000 tons; France, about 7000; and England about 60,000; while Italy imported 81,920 quintals of palm oil of the value of £216,270 in 1910 (78,460 quintals in 1908).

COCO-NUT OIL (or **Coco-nut Butter**) is obtained from the coco-nuts yielded twice a year by the palms *Cocos nucifera* and *Cocos butyracea*, which grow abundantly in Africa, Ceylon, Cochin China, and the Indies.

The coco-nut is oval and about 20 to 25 cm. long and 12 to 16 cm. broad; it is covered with a fibrous mass, used for making matting, cord, and baskets, and with a hard, woody shell, 8 to 12 mm. thick, which some time before maturation contains a sweetish, watery liquid (*coco-nut milk*), this subsequently disappearing and giving place to a soft edible pulp. The latter hardens in the air and is sold under the name of *copra* (60 to 70 per cent. of oil) for the extraction of oil. At the place of production this is carried out in a very primitive manner, but in European factories the dry pulp is ground, steeped in boiling water and pressed, first cold and then hot.

The oil is nowadays decolorised with bone-black or absorbent earths (magnesium hydrosilicates), and in the white form thus obtained is used as a comestible (*coco-nut butter*; *see* Margarine), after the free acids have been removed with highly concentrated solutions of caustic soda and after the odorous constituents have been expelled by means of superheated steam. The best form for use as food is the softer, almost liquid butter obtained by the first pressing in the cold. Its digestibility is equal to that of margarine and butter. If it contains more than 2 per cent. of free fatty acids (expressed as oleic acid), it cannot be used for food and then goes to the soap factory as industrial coco-nut oil.

Its composition is variable, and of the unsaturated acids it contains only oleic acid (about 10 per cent.), while glycerides of myristic and lauric acids are present in large quantities and those of caproic, caprylic, and capric acids to the extent of 2 to 3 per cent.

The pure fat contains no free fatty acids, or at most traces. It has already been mentioned that it gives a soap separable from solution only by very large quantities of salt; it is, however, capable of absorbing as much as 10 to 12 times its own weight of water, and is hence highly valued by soap manufacturers. It is used alone for culinary purposes and for mixing with margarine and adulterating cacao butter.

In its analysis, attention is paid to the physical and chemical constants given in the Table on p 378.

A large area of the earth's surface (about 1,400,000 hectares) is under coco-nut palms, which in a good year would yield 960,000 tons of coco-nut oil. In 1905 about 300,000 tons

of copra were placed on the market, and in 1906 only 200,000 tons, the average price being £19 per ton.

England imports, on an average, 34,000 tons of copra ; France, 100,000 tons, of the value of £1,400,000 (the exports are 10,700 tons) ; the figures for Germany are given above (*see* Palm-nut Oil). England imported 50,240 tons of crude coco-nut oil and 17,708 tons of the purified oil in 1909, and 53,968 tons of the crude and 50,021 tons (£1,136,736) of purified oil in 1910. The United States imported 25,000 tons of the crude oil in 1910 and 43,000 tons (£785,000) in 1911. Italy imported 344 quintals of coco-nuts in 1910 and also 20,225 quintals of coco-nut oil of the value of £66,340 (in 1908, 13,840 quintals). The Philippines exported 115,130 tons of copra in 1910, two-thirds of it to France.

VEGETABLE TALLOW (Chinese Tallow) is obtained by pressing the fruit (separated more or less from the seeds) of *Stillingia sebifera* (*tallow-tree*), which grows in China, Indo-China, &c. Pressing of the seeds (3 per fruit) yields *stillingia oil*, which is to some extent drying (iodine number more than 135). The tallow, however, serves well for making soap and has an iodine number of about 30, but this varies somewhat owing to variation of the amount of stillingia oil present. The tallow melts at 35° to 44°, and is sold in 40- to 50-kilo cakes wrapped in straw.

COTTON-SEED OIL is obtained by pressing the shelled, washed seeds of the cotton plant (*Gossypium herbaceum* and *barbadeuse*, cultivated in North America, and *G. religiosum*, *hirsutum*, and *arboreum*, cultivated in Egypt, India, China, Siam, &c.). The crude oil is reddish brown (sulphuric acid produces a red coloration) and is decolorised by stirring with 6 to 10 per cent. of a caustic soda solution of 10° to 15° Bé. and passing through it a vigorous current of air, first in the cold (40 to 50 minutes) and then when heated to 50° to 55° by indirect steam. It is then allowed to deposit, and is afterwards washed with 10 per cent. of salt water (at 10° Bé.) to remove the last traces of soap, decanted off, and passed through filter-presses to obtain it clear and of a fine straw-yellow colour. The fatty acids separated from the glycerides of cotton-seed oil contain about 26 per cent. of oleic acid, 47 per cent. of linolic acid (the oil is hence partly drying), and about 24 per cent. of saturated fatty acids (palmitic and up to 3 per cent. of a hydroxy-acid), besides a small proportion of an aldehydic substance (to which Becchi's reaction is due). It contains also 1·5 per cent. of a non-saponifiable sulphur compound and apparently a chloro-compound.

Tests for the detection of cotton-seed oil in other oils have already been described (p. 397), and the analysis of the oil is carried out with reference to the constants given on p. 378.

About two-thirds of all the cotton-seed oil is used directly or indirectly (as adulterant) as food ; the remainder (second and third qualities) serves, with palm oil and coco-nut oil, for making white soaps, although in some cases it gives rise, after some time, to yellowish spots.

The world's production of cotton being about 3,300,000 tons, that of cotton-seed should be 6,600,000 tons, but in reality is only 5,000,000 tons (three-fifths in the United States), and the United States produce about 500,000 tons of cotton-seed oil (2,725,000 barrels in 1909 and 3,000,000 in 1910, one-fourth of this being exported) and 1,100,000 tons of cotton-seed cake.

England produces about 70,000 tons of cotton-seed oil, imports 18,000 tons (1905) and exports about 18,000 tons. England imported 17,560 tons of cotton-seed oil in 1909 and 15,950 tons (£562,672) in 1910, and also 690,000 tons (£4,866,000) of cotton-seed in the latter year. In 1906, France imported more than 220,000 tons of the seed and 46,000 to 50,000 tons of the oil. The United States exported 85,000 tons (£2,638,200) of cotton-seed oil in 1910 and 155,000 tons (£4,367,800) in 1911. Germany imported about 17,000 tons of the seed and about 55,000 tons of the oil in 1904. In 1906 Austria imported 20,500 tons of cotton-seed oil. Italy imported 31,328 quintals of the oil in 1907, 108,117 quintals in 1908, 306,250 quintals in 1909, and 35,801 quintals—of the value of £117,430—in 1910.

MAIZE OIL (in America, Corn Oil) is now prepared in large quantities in America and Italy from maize germs, which are separated during grinding. These germs contain 40 to 50 per cent. of oil, and after being pressed hot leave an excellent cake for cattle-food (10*s*. to 12*s*. per quintal). The dense oil has a fine golden yellow colour and a faint odour of maize, and serves well for soap-making and for adulterating edible oils and linseed oil. That obtained by extracting the dried grains from spirit manufacture (*see* p. 153) is reddish brown, and is used for burning and as a lubricant when mixed with olive and mineral

oils, but is not used alone as it tends to resinify. As a drying oil it has no great value.

The fatty acids of the glycerides of maize oil are: stearic and palmitic (4 to 25 per cent.), oleic (about 40 per cent.), linolic and linolenic (about 45 per cent., so that the oil is partly a drying one), and small proportions of arachic, hypogæic, caproic, caprylic, and capric acids; the oil contains also about 1·2 per cent. of lecithin and 1·4 per cent. of non-saponifiable substances, mostly cholesterol or, more precisely, *sitosterol*, identical with that obtained from wheat and rye.

If in North America (Illinois) alone the oil were extracted from the germs of all the maize produced (about 6,000,000 tons—the world's total production being over 7,500,000 tons, 900,000 of this in Italy), more than 250,000 tons of the oil should be obtained. But only about 40,000 tons of maize oil are produced at the present time, about one-half of it being exported.

SESAMÉ OIL (Gingelly Oil, Teel Oil) is obtained from the seeds of *Sesamum indicum* (brown, oval, flat seeds, 4 mm. long, 2 mm. broad, and 1 mm. thick) and of *Sesamum orientale* (violet-brown or black), the latter giving as much as 50 per cent. of oil when pressed once in the cold and twice hot. The first oil expressed serves as a food for 250 millions of the inhabitants of India, where the area under sesamé exceeds ten millions of acres (*i.e.* 40,000,000 hectares). The exportation of sesamé seeds from India amounts to about 1,200,000 quintals annually, nearly all of this being directed to the Marseilles market, whence other countries are supplied. The Levant produces about one-tenth as much as India, and a little is produced in Africa, China, and Japan. In France the sesamé oil industry is declining owing to the obstinate empiricism of the older manufacturers and to the almost prohibitive Customs duties of various countries, but more than 1000 truckloads of the oil are still exported per annum. Germany imported in 1890 only 140,000 quintals of the seeds, but in 1903 615,000 quintals, and in 1905 nearly 465,000. Austria-Hungary imports on an average 150,000 quintals yearly. Italy imported 174,722 quintals of sesamé and arachis seeds in 1908, 309,000 in 1909, and 386,000, worth £617,400, in 1910.

Sesamé cake (dark or pale), so largely used as cattle-food, has the composition: water, 10 to 12 per cent.; protein substances, 37 to 39 per cent.; fat, 9 to 10·5 per cent.; and ash, 9·5 per cent.

Sesamé oil has a golden-yellow colour, that from the Levant being the paler; it consists of glycerides of stearic, palmitic, oleic, and linolic acids, 78 per cent. of the fatty acids being liquid with an iodine number of 140. The physical and chemical constants are given in the Table on p. 378, and the characteristic reactions for detecting it when mixed with other oils on p. 397. It is dextro-rotatory (+ 0·8° to + 2·4°).

The characteristic reactions, especially the colorimetric ones, are due to special components, such as *sesamin*; a lævo-rotatory alcohol, *sesamol*, $C_{26}H_{44}O, \frac{1}{2}H_2O$, which gives Baudouin's reaction (p. 384), and the methylene ether of hydroxyhydroquinone, $C_7H_6O_3$.

Sesamé oil is used in the manufacture of oleomargarine and soap and as burning oil.

ARACHIS OIL (Earthnut Oil, Peanut Oil) is obtained from the seeds of *Arachis hypogæa*, cultivated in Brazil, the Congo, and India, and to some extent in Spain, France, and Italy. The shelled seeds give 30 to 35 per cent. of oil. In 1908 Italy imported 4735 quintals of arachis oil, in 1909 46,833 quintals, and in 1910 50,820 quintals, of the value of £182,960. The oil obtained by the first cold pressing is almost colourless, has a slight flavour of beans, and is largely used as a comestible and for adulterating olive oil, although it readily turns rancid. The second pressing in the cold gives burning oil, and the third, in the hot, oil for soap-making. The liquid components contain *triolein* and *trilinolin*; the presence of hypogæic acid is uncertain; the solid constituents are composed of triglycerides of lignoceric acid, and to a less extent of arachic acid (5 per cent. of the oil). In olive oil arachis oil is detected by Renard's test, as modified by Tortelli and Ruggeri and by Fachini and Dorta (*see* p. 397).

SOJA BEAN OIL (Chinese Bean Oil) is extracted from the beans of *Soja hispida* (or *Soja japonica* or *Phaseolus hispidus*), which are cultivated in China and Japan (Formosa). The crushed beans are heated in jute bags over jets of steam and then pressed. A large part of the oil is used for soap-making. After purification by standing, the oil has a sp. gr. 0·9255 at 15°; acidity, 0; saponification number, 193·2; iodine number, 135; Hehner

number, 95·95 ; Reichert-Meissl number, 0·45 ; Maumené number, 86 to 87 ; index of refraction, 1·4750 at 20° ; solidification point, − 8° to − 16° ; melting-point of the fatty acids, 27° ; and solidification-point of the fatty acids, 22° (Oettinger and Buckta, 1911). The exportation of the oil from China amounts to 60,000 tons per annum.

GRAPE-SEED OIL. The seeds of the grape contain 10 to 20 per cent. of oil (more in white and sweet grapes). They are separated from the skins by drying in the sun or in ovens and then beating. The sieved seeds are dried completely, ground, steeped in 10 per cent. of water, heated, and pressed ; the cake is broken up, treated with 20 to 25 per cent. of water, and pressed again, this treatment being repeated so that all the oil may be extracted. The oil can also be extracted by means of solvents (benzine or carbon disulphide). When dark-coloured (extracted with solvents), it can be readily decolorised with animal-black. It has not a very pleasant odour and is rather bitter (if expressed in the hot).

This oil consists of glycerides mainly of linolic acid, together with those of solid fatty acids (10 per cent.), and a little erucic, linolenic, and ricinoleic acids. It has the sp. gr. 0·9202 to 0·9350.

It has slight drying properties and solidifies between −10° and −15° ; its saponification number is 178 to 180 ; iodine number, 94 to 96·5 ; Wollny number, 0·46 ; Maumené number, 52 to 54 ; and butyro-refractometer reading, 60 at 40°. The acetyl number of the fatty acids varies from 43 to 144, according to the extent of oxidation ; it thus resembles castor oil to some extent, so that it is recommended for the manufacture of sulphoricinate (*see* p. 327).

The pure oil expressed in the cold is used as a food, and the other varieties for soap-making. But if purified with sulphuric acid it serves well as a lighting oil, not so much on account of its luminosity, which is rather low, but more especially because it gives a smokeless flame.

After the removal of the fat, the *cake* contains 10 to 15 per cent. of water, 14 to 18 per cent. of protein substances, 8 to 10 per cent. of fat, and 6·5 to 7 per cent. of ash, and is used as cattle-food.

In Italy the extraction of grape-seed oil is capable of considerable development. A few factories have already been erected in Southern Italy and in the North ; some of the works treat a certain amount of the seed. Seeds obtained from distilled vinasse are somewhat diminished in value.

TOMATO-SEED OIL. In Italy 393,000 tons of tomatoes were produced in 1909 and 335,000 tons in 1910. In the province of Parma 84,000 tons are treated annually, and the residues (seeds, &c.) now yield 600 tons of oil (drying oil of the cotton-seed type). The refuse from tomato-ketchup factories (about 5 per cent. of the weight of the tomatoes) contains about 70 per cent. of aqueous liquid, 6 to 8 per cent. of dry skins, and 22 to 24 per cent. of dry seeds.

One hundred kilos of tomatoes give 95 kilos of liquid juice, which is concentrated for preserve, and 1 per cent. of dry seeds containing 23 per cent. of oil, 18 per cent. (180 grms.) being extractable by pressure ; the remaining 820 grms. consists of *cake* (5·2 nitrogen, 12 per cent. fat, 22·7 per cent. cellulose, 21 per cent. non-nitrogenous extractives, 6·5 per cent. ash, 0·22 per cent. of dry skins, and 3 78 per cent. of aqueous liquid adhering to the moist residues).

The oil expressed in the cold from sound seeds is straw-yellow, and with 20 per cent. of tallow gives a good washing soap.

Analysis of the oil gives the following results (Fachini) : density at 15°, 0·9215 ; refractive index, 1·4765 ; acid number, 0·46 ; saponification number, 191·6 ; iodine number, 114 ; iodine number of the fatty acids, 122·7 ; iodine number of the liquid fatty acids, 142 2 ; Hehner number, 93·8 ; acetyl number, 20·4.

TREATMENT OF FATS FOR THE MANUFACTURE OF SOAP AND CANDLES

Candles are mostly made from solid fatty acids (stearic and palmitic) obtained by decomposing fats and oils into glycerine and fatty acids and pressing from the latter the liquid fatty acids, which are used, either alone or together with the solid acids, for soap-making. Liquid oils and soft fats, which contain little stearic and palmitic acids, are

hence used not for candles but only for soap, but the stiffer fats are often treated in one and the same works for making candles and soap.

The resolution of fats into acids and glycerine is carried out in very varied ways: by means of lime, sulphuric acid, superheated steam, or biological or catalytic methods.

(1) **Saponification with Lime and Separation of the Solid Fatty Acids.** Theoretically 100 kilos of fat (*see* p. 377) require 9·5 kilos of lime for hydrolysis, but when this process was first used industrially by Milly in 1834 as much as 15 per cent. of lime was used, so that a very large amount of sulphuric acid was consumed in liberating the fatty acids from the calcium soaps formed, while fatty acids were carried down by the enormous quantities of calcium sulphate formed and hence lost.

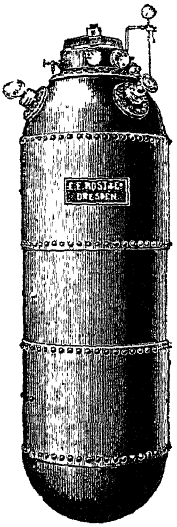


FIG. 268.

On this account the process was not used, but Milly showed later (1855) that, by heating in an autoclave under pressure instead of in open pans, the amount of lime could be reduced to 2 to 3 per cent.—that is, less than the theoretical quantity—and yet practically complete saponification effected (*see* p. 370). Indeed, after 1 hour 64 per cent. of the fat remained unsaponified; after 2 hours, 24 per cent.; after 4 hours, 15 per cent.; after 6 hours, 9 per cent.; after 9 hours, 2 per cent.; and after 12 hours, 0·7 per cent.

The saponification is now carried out in large vertical copper autoclaves (Fig. 268) (5 to 6 metres high, 1 to 1·2 metre in diameter, of sheet copper 15 to 20 mm. thick), into which are passed several quintals (up to 20) of the fused fat from the tank, *A* (Fig. 269), and then about one-third as much milk of lime, containing 2 to 3 per cent. of lime (calculated on the fat), from the vessel *B*. The heating is continued for 6 to 8 hours at a pressure of 8 to 10 atmos., steam free from air being passed in, first at low pressure from the generator, *D*, and then at high pressure (10 to 12 atmos.) by the tube, *e* (Fig. 270), reaching to the bottom of the autoclave and terminating in a perforated coil. The steam alone keeps the mass mixed without the special stirrers formerly used, if the precaution is taken of allowing a little steam to escape continually from a tap at the top. At the end of the operation the steam is shut off, and when the temperature has fallen to 125° to 130° (about 3·5 atmos. pressure) the internal pressure is utilised to discharge first of all the aqueous glycerine from below by opening the valve, *c*, connected with a tube reaching to the bottom of the autoclave. In a similar manner the fused and subdivided calcium

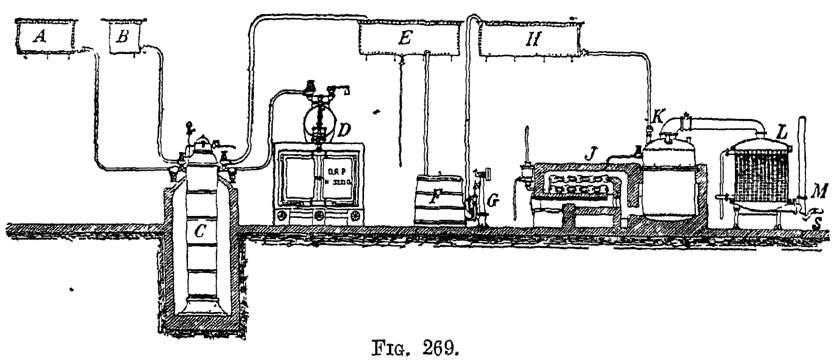


FIG. 269.

soap mixed with free fatty acids is forced into the tank, *E*, where a further quantity of aqueous glycerine separates, or the calcium soap is passed directly to the lead-lined vessels, *F*, where it is decomposed by a sufficient quantity of sulphuric acid to neutralise all the lime added.[1] After shaking, the gypsum is deposited and can be separated, and the fatty

[1] During recent years several factories have replaced lime by *magnesia* (calcined natural carbonate), which possesses various advantages: when it is used in the proportion of 1·5 to 2 per cent., a pressure of 4 to 5 atmospheres is sufficient to produce complete saponification, since the magnesium soap formed gradually emulsifies and almost dissolves in the remaining fat which is thus easily resolved by the water and magnesia. Then, too, decomposition of the magnesium soap with sulphuric acid, instead of giving an insoluble and useless salt (calcium sulphate, which always retains a little fat), gives magnesium sulphate, which is soluble in water, readily separable

acids, which float, are washed several times with hot water and then, if the fatty acids are distilled—as is done in certain factories where dark fats are treated—they are forced by a pump, *G*, to the tank, *H*. The latter feeds a cast-iron or copper (this is considerably attacked) boiler, *K*, which is heated partly by almost direct-fire heat and partly by superheated steam (at 180° to 230°) passed into the interior from the superheater, *J*. The steam carries the fatty acids, which distil, into the tinned copper condensing coil, *L* ; these acids finally collect in a white condition, together with condensed water, in *S*, while the non-condensed gases are evolved from the tube, *M* (*see* later : Decomposition with Sulphuric Acid).

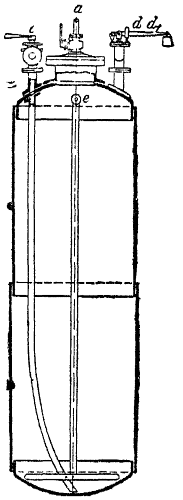


FIG. 270.

Where the fatty acids are not distilled, they are solidified by passing them into a number of superposed tin-plate pans (Fig. 271) fed by the tubes, *D*, from the fused fatty-acid tank, *F*. When all the pans are full, the tubes, *D*, are closed with wooden plugs, *E*, and in 24 hours many of the pans contain solid cakes, consisting of a mixture of solid stearic and palmitic acids and liquid oleic acid. In order to separate the latter, the cakes are wrapped in woollen or camel's-hair or goat's-hair cloths and are then placed between metal plates and pressed, first in the cold with a pressure gradually increasing to 200 to 260 atmos. A second pressing at 40°, either in the same press or in a horizontal press, results in the almost complete separation of the oleic acid, which, however, retains in solution a little palmitic and stearic acids. The latter acids are separated by cooling the oleic acid and, after some time, filtering or decanting off the *oleine* (p. 298), which is then put on the market or used for soap-making.

The solid white cakes of stearic and palmitic acids, freed from the dark edges, bear the commercial name of *stearine* and melt at 56° to 56·5°. These are often melted again, washed with warm water, poured into pans to solidify, and then pressed hot in hydraulic presses so as to remove the final portions of oleic acids ; this product, known as *double stearine*, melts at 57·5° to 58°.

The solidification of the crude acids, after liberation by sulphuric acid, is now effected more rapidly and more perfectly by passing the fused acids at *g* (Figs. 272 and 273) into a casing into which dips a large, rotating, double-walled cylinder. Between the walls flows a non-congealing solution like that from an ice machine (*see* vol. i, p. 231), and the layer of fatty acid solidifying at the surface is detached by means of a scraper, *h*, and falls into a cooled box, *F*, connected with the pump, *P*, and functioning as a filter-press. This process of the firm of Petit Frères has now been improved by replacing the cylinder by a highly cooled toothed wheel. In some cases, also, channelled cylinders are used, whilst in others the liquid fatty acids are withdrawn from the cold pasty mass containing the mixture of liquid oleine and the stearine in small crystals, by immersing in the mass a rotating vertical cylinder formed of metallic gauze and covered with a well-stretched cloth ; inside the cylinder the pressure is reduced by means of a suction-pump, so that the liquid oleic acid is sucked in, while the stearic acid is gradually scraped from the surface of the cylinder and pressed in a hydraulic press.

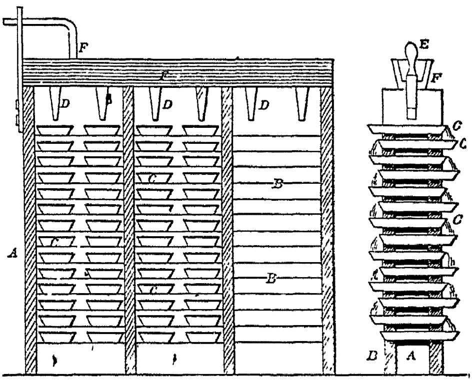


FIG. 271.

Messrs. Lanza Bros. of Turin, instead of separating the liquid from the solid fatty acids by means of hydraulic presses, suggest emulsifying and dissolving the liquid acids with solutions of sulpho-oleic acid, so that they separate at the surface, while crystals

by simple decantation and in some cases utilisable. For similar reasons, *zinc oxide* is now used in some of the Italian factories. Bottaro (1908) has suggested the use of sulphurous anhydride to decompose the calcium soap from the autoclave.

of the solid fatty acids collect underneath (Ger. Pat. 191,238). The sulpho-oleic acid is prepared by shaking 100 parts of oleic acid with 50 parts of sulphuric acid of 66° Bé. in the cold and then diluting with 4000 parts of water.

The decomposition of fats by lime in an autoclave at not too high a pressure has the advantage of giving the fatty acids in a sufficiently clear condition to render distillation useless; the resulting glycerine and stearine are also clear.[1]

(2) **Decomposition with Sulphuric Acid** (proposed by Achard in 1777 and then by Frémy in 1836). This method is now used more especially for very dark fats, which should, however, be freed from impurities, dried by fusion at 120°, and decanted after long standing. The fused fat is introduced into a double-walled, lead-lined, copper or iron boiler fitted with a hood for carrying off the sulphur dioxide which is always evolved. According to the nature of the fat, it is heated with 5 to 10 per cent. of concentrated sulphuric acid at 120° for 1 to $1\frac{1}{2}$ hour, steam being passed through the jacket and the mass kept mixed by a current of air passing through it. The operation is finished when a test portion, placed on a dark plate, crystallises on cooling; the mass is then passed into large wooden vats and heated with water until the emulsion first formed is resolved into two layers, the glycerine below (this is separated and freed from sulphuric acid by means of lime) and the acids above. The latter is subsequently boiled several times with water until the excess of sulphuric acid is removed, the sulphuric ethers of oleic acid being decomposed with formation of solid hydroxystearic acid. The resulting fatty acids are dark in colour, since they retain in solution the impurities of the fat partially carbonised by the sulphuric acid; to purify and whiten them, they are distilled with superheated steam, as described above (*see also* Fig. 269); the first and last portions which distil are the more coloured and these are redistilled. Hirzel (Ger. Pat. 172,224, 1906) has devised an arrangement for continuous distillation, all that is required being a boiler of moderate size into which the crude fatty acids are run in a constant stream; the pure acids distil over, while the *tar* remaining at the bottom of the boiler is discharged.

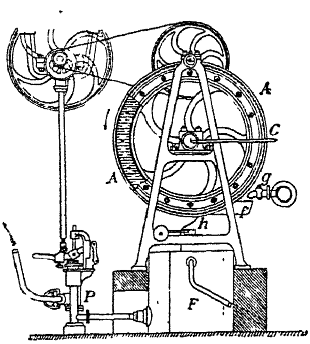


FIG. 272.

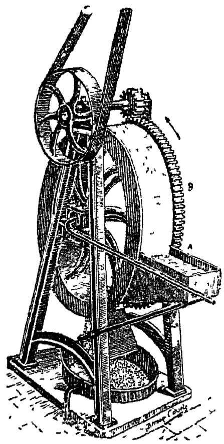


FIG. 273.

Redistillation of this *tar* gives a final residue of black *stearine pitch*, amounting to about 2 per cent. of the fatty acids distilled. In some works the fatty acids are distilled in a vacuum at a temperature not exceeding 240°, higher temperatures than this giving a coloured product; the acrolein and hydrocarbons given off are condensed.

The fatty acids obtained by distillation are separated into liquid and solid by pressure in hydraulic presses, liquid *distilled oleine* and white, solid *distilled stearine* being thus obtained. This oleine always contains a little acrolein and hydrocarbons, as the crude fatty acids which are distilled invariably include a small proportion of non-saponified neutral fat. On the other hand, distillation results in the formation of an increased amount of solid fatty acids (about 15 to 18 per cent.), since sulphuric acid converts oleic

[1] During recent years, industrial application has been made of the Krebitz process (Ger. Pat. 155,108, 1902), which is a simplification of the lime process with direct production of soda soap, and is attended by considerable saving in fuel, caustic soda, and plant. To the fused fat is added the necessary quantity of lime (10 to 12 per cent. CaO) mixed to a paste with three to four times its weight of water, the mass being well mixed, boiled for five minutes, covered, and allowed to stand overnight. By this means saponification is complete and a calcium soap is obtained which can be readily ground up in a mill. When this is washed in a vat with a perforated bottom, the first portion of hot wash-water removes the major part of the glycerine as a solution of 10 to 20 per cent. concentration, while a second washing gives a more dilute glycerine solution which is used for the first washing of the calcium soap of a subsequent operation. When treated in the hot with sodium carbonate solutions, the calcium soap yields soda soap and calcium carbonate, which require skilled manipulation for their proper separation. In this case also, fusion and treatment with hot water is employed for the complete removal of impurities. This process is not applicable to the manufacture of soft soaps.

acid partly into the corresponding sulphuric ether, which yields solid hydroxystearic acid when boiled with water:

$$C_{17}H_{33}\cdot CO_2H + H_2SO_4 = C_{17}H_{34}<^{CO_2H}_{O\cdot SO_3H}$$

$$C_{17}H_{34}<^{CO_2H}_{O\cdot SO_3H} + H_2O = H_2SO_4 + C_{17}H_{34}<^{CO_2H}_{OH.}$$

During the distillation with superheated steam, the *hydroxystearic acid* is transformed almost entirely into iso-oleic acid (*see* p. 299). It must, however, be borne in mind that hydroxystearic acid is not very good for making candles, as it accumulates in a fused state in the cup formed by the burning candle round the wick; further, when melted with stearic acid it tends to separate in layers instead of giving a homogeneous mass.

In order to obtain a greater proportion of solid fatty acids, some works combine these two systems of saponifying by means of lime and acid. The saponification is first carried out in autoclaves in the ordinary way, but not to completion, the acids and the remaining fat (4 to 5 per cent.) being then separated by means of sulphuric acid; the fatty acids and fat are dried and completely saponified with 2 to 2·5 per cent. of concentrated sulphuric acid at a temperature of 110° to 120° maintained for an hour. The resulting fatty acids are not distilled but are simply washed with boiling water, being thus rendered rich in solid hydroxystearic acid; this process also yields a *much* purer glycerine.

L. Fournier (Fr. Pat. 262,263) has suggested a method of increasing the amount of solid fatty acids by effecting the sulphonation with concentrated sulphuric acid in a carbon disulphide solution of the fat, the reaction then proceeding immediately without heating.[1]

(3) **Hydrolysis by Hot Water under Pressure** (proposed by Tilghmann in 1854) is but little used owing to the low yields obtained and the very high pressures required. The fat, emulsified with water, is circulated in coils arranged in a furnace so as to attain a temperature of 300° to 350°.

Direct distillation of fats with superheated steam and collection of the glycerine and fatty acids in the distillate always gives low yields.

(4) The **Biological** or **Enzymic Process** has been applied industrially since 1902, as a result of the work of W. Connstein, E. Hoyer, and H. Wartenberg, and is based on the observations of Green and of Sigmund (1891) according to which, when oily seeds are pounded with water, fatty acids are gradually liberated by the action of lipolytic enzymes (*see* p. 112). It is found that the most active enzymes are those of castor oil seeds (in which they occur to the extent of 70 parts per 1000 of fat), especially after removal of

[1] **Transformation of Oleic Acid into Solid Fatty Acids.** For some years (about 1877–1885), *oleic acid was converted* on an industrial scale in France and England (by the process of Olivier and Radisson) *into solid palmitic acid* by utilising Varrentrapp's reaction, according to which this change is almost quantitative on fusion with solid caustic potash (*see* pp. 290 and 299): $C_{18}H_{34}O_2 + 2KOH = H_2 + CH_3\cdot CO_2K + C_{16}H_{31}O_2K$. But the greasiness and unpleasant odour of the candles obtained compared with those made from stearine, the necessity of distilling the resultant dark acid, and the difficulty of eliminating all the acetic acid, led to the abandonment of this process. Also *de Wilde and Reychler's process for transforming oleine into stearine* by heating in an autoclave at 260° to 280° with 1 per cent. of iodine or chlorine or bromine seems to have been given up in practice since 1890, the yield being less than 75 per cent. (the combined chlorine was eliminated by heating under 8 to 10 atmos. in presence of zinc dust or iron, and then decomposing the metallic soap).

The industrial transformation of *oleic acid into solid elaidic acid* by treatment with a little nitrous acid (*see* p. 299) does not give satisfactory practical results, first because elaidic acid is not a very good material for candle-making, and also because the reaction succeeds well only with fairly pure and *fresh* oleic acid and not with the commercial acid (partly polymerised). Max v. Schmidt treats 10 parts of oleic acid with 1 of zinc chloride at 180°, then decomposes the zinc soap by boiling first with dilute HCl and afterwards with water and finally distils the fatty acids, which can be separated into liquid and solid by means of hydraulic presses. By this process Benedikt (1890) obtained 75·8 per cent. of *stearolactone*, $C_{18}H_{34}O_2$ (the internal anhydride of *γ-hydroxystearic acid*), 15·7 per cent. of iso-oleic acid, and 8 5 per cent. of other saturated acids.

K Hartl, jun. (Ger. Pat. 148,062, 1903), in order to avoid the browning produced by the action of sulphuric acid on the impurities of the oleic acid, does not treat the oleine directly with concentrated sulphuric acid (as had long been the custom; *see* Shukoff, Ger. Pat. 150,798, 1902), but first distils the oleic acid in steam and afterwards treats it with sulphuric acid of 58° to 60° Bé. (*e.g.* at a temperature of 60° to 80° and using 1 mol. of sulphuric acid per 1 mol. of oleic acid); the resulting fatty acids are then washed and decolorised by heating in open pans with 1 to 10 per cent. of zinc dust at 100°, the zinc soap being finally decomposed by hot dilute hydrochloric acid. W. H. Burton (U.S. Pat. 772,129, 1904) uses a process similar to that of Fournier (*see above*), benzine or naphtha being employed as solvent and the sulphonic ethers being decomposed in solution by the direct action of steam.

The general reaction of Sabatier and Senderens (*see* pp. 34 and 59) has also been applied practically (Ger. Pat. 141,029, 1902), a current of hydrogen being passed into the hot mixture of oleic acid and catalytic powdered nickel (reduced nickel) (*see also* E. Erdmann, Ger. Pat. 211,669, 1907); if the oleic acid is pure, it is transformed almost completely into stearic acid. A similar reduction, but with a lower yield, is obtained with the electric discharge (Ger. Pat. 167,107, 1904). A. Knorre (Ger. Pat. 172,690, 1903) treats an emulsion of oleic acid and formaldehyde with zinc dust.

the oil. But better results are now obtained by using aqueous emulsions rich in enzymes (*extract of castor oil seeds*), but much poorer in proteins (which are harmful) and containing 60 per cent. of water, 37 per cent. of castor oil, and 3 per cent. of proteins. When the seeds are used, a milky emulsion is obtained by crushing the seeds in presence of the necessary amount of water (50 to 60 per cent.) and is decanted off roughly from the skins and treated with 0·06 per cent. of acetic acid (calculated on the weight of fat to be decomposed subsequently). Of the seeds or the enriched extract, 50 to 80 kilos are used per 1000 kilos of fat (the maximum for fats with the higher saponification number; although tallow requires the maximum amount and a temperature of 40°). To accelerate the decomposition, 0·15 to 0·20 per cent. (on the weight of fat) of manganese sulphate (*activator*) dissolved in a little hot water is added, and if the fat contains much protein or gummy matter, it is well to clarify it by heating with 1 per cent. of sulphuric acid diluted with a little water; the last traces of this acid are then removed by repeated and thorough washing with water, as they would be deleterious to the reaction. With liquid fats, the decomposition is carried out at 23° and with solid ones at 1° to 2° above the melting-point, provided however that this does not exceed 42°, since at 44° the enzymes no longer act in the desired direction; if necessary, fats with high melting-points are mixed with liquid oils.

The practical working of the process is as follows: A leaden coil for indirect steam and a tube for the injection of air reach almost to the bottom of a lead-lined iron boiler with a conical base; discharge cocks are fitted to the boiler at the bottom and at various heights. The fat and about 35 per cent. of water are heated to the desired temperature (*see above*), being kept stirred by means of a current of air. The castor-seed extract, mixed with 0·2 per cent. of manganese sulphate and 0·06 per cent. of acetic acid (on the weight of fat; the reaction starts and proceeds well if the mass is faintly acid at first) is then added, the whole being mixed for about 15 minutes so as to give a homogeneous emulsion. The vessel is then tightly covered so that the temperature may be maintained, the mass being mixed from time to time to keep it emulsified. After 24 to 36 hours, when more than 90 per cent. of the fat is decomposed, the mass is mixed and heated to 80° to 85°, 0·2 to 0·3 per cent. (of the weight of fat) of concentrated sulphuric acid (66° Bé.) diluted with one-half its weight of water being then added. The whitish emulsion soon becomes dark owing to the separation of the fused fatty acids and when this occurs the heating and stirring are suspended and the mass left overnight. The various taps are then set in operation to separate the bottom layer of fairly concentrated glycerine, the intermediate emulsified layer (3 to 4 per cent. of the fatty acids, used for soap-making) and the clear fused fatty acids which are boiled with water to free them from sulphuric acid. Originally, when the seeds were used instead of the extract, the resulting glycerine was very dark, and it was necessary to decolorise it with bone-black (nowadays it is as good as that given by saponification with lime), while the intermediate emulsified layer formed as much as 22 per cent. of the total fatty acids (now only 2 to 4 per cent.). The *aqueous glycerine* (*sweet water*) of the enzymic process is first concentrated to 10° Bé. in open pans, the sulphuric acid being separated by means of barium carbonate in the hot. The barium sulphate is removed by filter-pressing and the filtered liquid further concentrated in a multiple-effect vacuum apparatus to 28° Bé., a clear, brownish glycerine containing only 0·2 to 0·4 per cent. of ash being thus obtained.

The biological process has spread rapidly during recent years, since the whole of the glycerine is readily recovered, while the fatty acids obtained are of far better quality than those prepared by decomposing the fat in autoclaves by means of lime, &c. The fatty acids from sulphocarbon olive oil retain, however, their characteristic green colour, and those from palm oil their orange colour. The fatty acids yielded by this process contain neither hydroxy-acids, as do those obtained under pressure, nor calcium soaps, and are hence more suitable for the manufacture of either candles or soap (*see later*, Soap).

(5) **Twitchell's Catalytic Process.** The decomposition is here analogous to that with sulphuric acid (which also, strictly speaking, is catalytic), but with *Twitchell's reagent* (*benzenestearosulphonic acid*) it takes place far more readily probably because this reagent dissolves in the fat more easily than does sulphuric acid. The fats are first purified by heating to 90° to 100° in a lead-lined covered vat (Fig. 274) with 1·5 to 2 per cent. of sulphuric acid at 60° Bé., direct steam being passed in so that when the acid is discharged after standing overnight it has a specific gravity of 8° Bé. (for cotton-seed or linseed oil,

15° Bé.). The purified fat is passed into another wooden vat, *B*, provided with a wooden cover, one half of which is removable; it is here mixed with 20 per cent. of distilled or condensed water (from the tank *G*), the mixture being then boiled by direct steam and 0·5 to 0·15 per cent. of the Twitchell reagent added (the minimum with pure fats and the maximum with highly impure third-grade fats). The current of steam is continued so that a homogeneous emulsion is rapidly obtained, and after being heated in this way for 24 hours about 90 per cent. of the fatty acids are liberated and the glycerine separated. No more steam is then passed through the mass, but a slow jet is kept flowing into the space between the surface of the liquid and the cover to prevent the fatty acids from turning brown during the subsequent operations owing to contact with the air. In about an hour's time, the emulsion breaks up and the fatty acids float on the aqueous glycerine; if the emulsion should not disappear, it is mixed gently for a few moments with 0·1 to 0·2 per cent. of sulphuric acid of 60° Bé. and then left. The sweet water usually has a specific gravity of 5° Bé. (15 per cent.) and forms 50 per cent. of the weight of the fat, and if this is not the case, the quantity of distilled water added initially and the dryness of the steam employed are varied when further quantities of fat are treated. The sweet water is neutralised with lime and concentrated (*see* p. 185). For soap-making the fatty acids may be used as they are, but as a rule the saponification is completed by adding 10 per cent. of pure water and heating for 12 to 24 hours with direct steam, any small amount of emulsion formed at the surface of the liquid by the steam being destroyed by the addition of a little sulphuric acid. In this way, 97 to 98 per cent. of the theoretical amount of fatty acids is obtained. Barium carbonate (1 part per 10 parts of Twitchell's reagent used, or more if sulphuric acid were added to destroy emulsion), mixed with a little water, is now added, and the whole heated for 15 to 20 minutes; if the lower layer of water now has an acid reaction towards methyl orange, more barium carbonate must be added. The current of steam, both in and above the liquid, is now stopped, since after this the fatty acids are no longer turned brown by the air. The sweet water drawn off after clarification is very dilute and is used in place of water in the treatment of further quantities of fat. After crystallising and pressing to separate the solid from the liquid acids (*see above*), the fatty acids are now ready for converting into soap and candles. In general they are less coloured as the amount of Twitchell's reagent used and the duration of its action are diminished. Good results are not obtained until after five or six operations, by which time the surface of the wooden vessels ceases to be attacked.

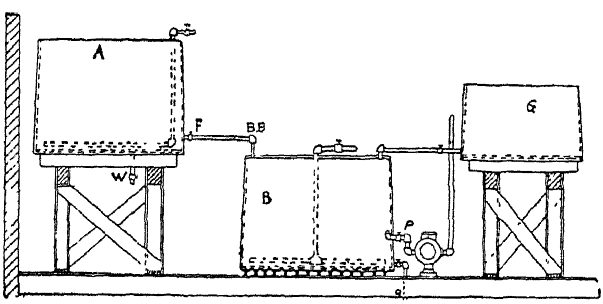


FIG. 274.

Just as with the preceding process, the use of the Twitchell process has spread considerably in America and in Europe.[1] The Twitchell reagent (which costs about 1*s*. 2*d*. per kilo) and estimates for the plant may be obtained directly from Messrs. Joslin, Schmidt & Co., 3223 Spring Grove Avenue, Cincinnati, Ohio, or from their representatives in various countries.

[1] The plant for a factory using the biological or catalytic process is considerably less expensive than for one employing autoclaves, while there is also a decided economy in the working expenses, as is shown by the following approximate figures, which show that these processes are of value, at any rate in countries where coal is dear. These data are from a large factory using the Twitchell process and treating about 70,000 kilos of fat per day—10,000 kilos at a time in each apparatus The prices given are those current in Italy, and the cost is calculated for 100 kilos of fat treated; the figures in brackets give the corresponding cost for the autoclave method: coal at 40 lire (32*s*.) per ton, 0 20 lira (0·82 lira); sulphuric acid, 0·09 lira (0·37); baryta or lime, 0·06 lira (0 11); labour, 0 03 lira (0·04); depreciation and repairs, 0 02 lira (0 26); Twitchell reagent, 0·80 lira. Hence the total cost of treating 100 kilos of fat will be at most 1·20 lira (11½*d*.) with the Twitchell process and at least 1·60 lira (15 4*d*.) with the ordinary autoclave process. In the case of small plants, the cost of working increases somewhat with the Twitchell process, but there is always an advantage owing to the less initial outlay required.

MANUFACTURE OF CANDLES [1]

The prime materials for the manufacture of candles are the combustible fatty matter and the wick.

A good candle should give a white light, should burn slowly, should not "gutter" or diffuse an unpleasant smell, should not be greasy to the touch, should be white and give a smokeless flame, and should not splutter, while the relation between the size of the wick and that of the candle must be properly chosen.

The object of the *wick* is to feed the flame regularly with the melted material. It is usually made of filaments (15 to 20) of pure cotton or linen without knots. Animal fibres should be rejected, as they give an unpleasant smell and a fused carbonaceous mass which diminishes the luminosity. Wicks formed of filaments which are only twisted require frequent snuffing, since they do not bend on themselves and do not burn completely, whilst, if they are *plaited* or woven and twisted, as Cambacères proposed, this inconvenience is overcome. For stearine candles obtained by fusion, the wick is of twisted cotton braid, while for more readily fusible materials (wax, tallow, &c.), more or less twisted wicks are used according as the candles are made by fusion or by compression. Nowadays wicks are made with suitable machines like those used for knitting, these effecting also the twisting of the filaments.

Wicks which have not been *pickled* do not act well for candles, as they leave a carbonaceous residue which diminishes their capillary property.

In 1830, Milly found that the combustion of the wick is facilitated by steeping it in a solution of boric or phosphoric acid, such treatment being, however, only of advantage with braided wicks.

Many other substances have since been proposed for this purpose. Thus, in France the wicks are immersed for 3 hours in a solution of 1 kilo of boric acid in 50 litres of water, and are then pressed, centrifuged, and dried; in some cases a *trace* of sulphuric acid is added to the bath. In Russia, the wick is left in a solution of sulphuric acid (50 grms. per litre), squeezed, dried in hot air, steeped in a bath containing 4·5 grms. of boric acid and 18 grms. of ammonium sulphate per litre of water, and then dried. Another solution giving good results is composed of 60 grms. of borax + 30 grms. KCl + 30 grms. KNO_3, + 30 grms. NH_3 + 3·5 litres of water. The borax renders the flame white.

In general these products either induce a more ready oxidation (chlorates, nitrates) or melt the ash of the wick, which thus gradually falls by its own weight. In some cases the penetration of the solution into the wick is hastened by the addition of a little alcohol.

If the candle is too large in comparison with the wick, the excess of stearine melts and forms a kind of cup with tall sides full of the fused stearine, which cannot be completely absorbed by the wick and so makes the flame smaller; then, when the edges fall, the stearine overflows and produces guttering. If, on the other hand, the wick is too large, an insufficient quantity of wax is melted and no cup is formed to contain it, the candle guttering continually from the sides and the flame being less luminous.

[1] The ancient Romans used for illuminating purposes a kind of torch steeped in wax or bitumen. Only after the second century of the Christian era was a distinction drawn between wax candles and those of tallow; the use of the latter was regarded as a luxury, while wax candles were employed in churches. The Catholic religion used them exclusively for religious functions, and thus caused a great increase in the consumption, which diminished only after the spread of the Reformation. Very soon, however, the consumption of wax candles again increased very considerably owing to their extended use at the courts of kings and princes. Meanwhile the employment of tallow candles for domestic purposes was continually spreading, and in the eighteenth century several important factories were working in England; but the candles produced were high in price and burned very quickly. Only after Chevreul's work on the nature of fats in the early part of last century (after 1815) led to improvements in the saponification and to the preparation of solid fatty acids was the rational manufacture of candles initiated. Chevreul himself, together with Gay-Lussac, patented in 1825 a process for preparing candles from stearic acid; but the resulting industrial undertakings were soon abandoned, owing to the difficulties encountered in the saponification and in the preparation of the wick. It was only when Cambacères, in 1830, devised plaited and twisted wicks, and when Milly, in 1834, introduced saponification with lime and the subsequent decomposition of the calcium soap with sulphuric acid, that the manufacture was placed on a stable and remunerative basis. Milly's first factory for stearine candles was erected in Austria in 1837, and in 1840 one was started in Berlin and another in Paris. Important improvements were made in 1842 by saponifying the fats with sulphuric acid, and in 1854 by saponifying the fats and distilling the fatty acids with superheated water or steam (processes of Tilghmann, Berthelot, and Melsen). Almost immediately after this, however, the manufacture of paraffin candles was started, paraffin having been obtained in large quantities by Young (1850) by the dry distillation of bituminous coal (boghead, &c.), peat, shale, lignite, &c.; this industry underwent further extension after paraffin had been extracted from petroleum and ozokerite (*see* p. 80).

In 1904 a patent was filed for the manufacture of *artificial silk* candle-wicks, which seem to give good results.

Formation of the Candles. The white blocks of stearic and palmitic acids from the presses are scraped at the surface and edges to remove adherent impurities. The purer residue is melted and shaken in a leaden vessel with sulphuric acid (3° Bé.) to dissolve and separate the impurities (iron, hairs from the press bags, &c.); the sulphuric acid is then decanted off and the stearine washed repeatedly with boiling water to remove all trace of the mineral acid. In some cases the fused fatty acids are shaken with a little albumin, being then allowed to stand so that the coagulated albumin and the impurities may settle. In cooling, the stearine tends to crystallise, the resultant candles being then less homogenous and more brittle, At first arsenious acid was used to prevent crystallisation, but, now that this is prohibited, the stearine is kept continually shaken until it almost solidifies when it is introduced into the moulds, and the candles then rapidly solidified. It is often more convenient to add a little white wax or paraffin (2 to 10 per cent.), which also prevents crystallisation of the stearine.

a

FIG. 275.

The quality and purity of the stearine are ascertained by the usual tests, the neutral fat being determined by Geitel's test (*see* p. 379), the paraffin, cerasin, cholesterol, and carnauba wax by the saponification number and by the non-saponifiable matter (*see* p. 379), and the amount of oleic acid by the melting-point (which is 56° to 56·5° for pure stearine *pressed once* and 57·5° to 58° for *doubly pressed stearine*) and the solidification point, making use of de Schepper and Geitel's Table[1] obtained by mixing saponification stearine, solidifying at 48°, with oleine having a solidifying point of 5·4°.

Candles are made in three different ways: (1) *by immersion*; (2) *by fusion*; and (3) *by pressure.*

The first of these methods is the oldest and is now almost entirely abandoned. It was employed originally for *tallow candles,* and is now sometimes used to mask the presence of inferior fat or stearine, the wicks suspended from frames being first immersed in the impure fused fat, while the outer layers are obtained by dipping into a purer fat or fatty acid.

In China considerable use is still made of tallow candles of peculiar shape with a hole in the middle.

Certain long tapers are obtained by pressure, the semi-fused wax or stearine and the wick being forced through a tube.

But almost all candles are now made by fusion in highly perfected machines, which admit of a maximum output being rapidly obtained with a minimum of labour. The moulds, which are very smooth inside, have the shape of the candles—with the pointed end below and the enlarged base at the top (Fig. 275)—and are imperceptibly conical; they are made of an alloy composed of 3 parts of tin and 1 part of lead. For the fusion of a large number of candles at a time (100 or more) a machine is used similar to that shown in Fig. 276. The moulds of all the candles pass through the closed metallic box, *E D*, to the bottom and cover of which they are screwed. Tepid or cold water can be passed

[1] *De Schepper and Geitel's Table of the solidifying points of mixtures of fatty acids:*

Temperature of solidification	Per cent. of stearine	Temperature of solidification	Per cent. of stearine	Temperature of solidification	Per cent. of stearine	Temperature of solidification	Per cent. of stearine
5 4°	0	16°	7·7	27°	21·7	38°	50·5
6°	0 3	17°	8 8	28°	23 3	39°	54 5
7°	0 8	18°	9·8	29°	25·2	40°	58·9
8°	1 2	19°	11·1	30°	27·2	41°	63·6
9°	1 7	20°	12·1	31°	29·2	42°	68·5
10°	2 5	21°	13·2	32°	31·5	43°	73·5
11°	3 2	22°	14·5	33°	33 8	44°	78·9
12°	3 8	23°	15·7	34°	36 6	45°	83·5
13°	4 7	24°	17	35°	39 5	46°	89 0
14°	5·6	25°	18·5	36°	43·0	47°	94 1
15°	6 6	26°	20·0	37°	46·9	48°	100 0

at will through the box at *I* or *H*, so as to surround the moulds. The lower part of each mould contains a kind of small piston which has exactly the shape of the point of the candle and can be made to traverse the whole length of the mould, being joined to an iron tube, *B*, fixed to a frame capable of being raised and lowered by the rack and pinion, *C*. All the pistons can be raised at once so as to force all the solidified candles from the moulds. In order that the wick may be always in the middle of the candle, it is wound on bobbins, *A*, and passes through the iron tube which raises the piston to the upper part of the mould. The semi-fused, opalescent stearine, which is poured into the moulds kept by means of warm water (45° to 60°) at a temperature slightly above the melting-point, is then cooled by passing cold water round the moulds. When solidification is complete, the enlarged bases at the top of the candles are cut off by a knife and the candles forced out and grasped by the rods, *L*. In rising, the candles unwind from the bobbins new wicks which are thus brought into the middle of the moulds ready for the next operation. When the second batch of candles is solidified in the moulds, the wicks of the first batch are cut so as to make way for the others to be removed from the moulds. When shorter candles are required, the pistons are raised in the moulds to the desired height and the stearine then run in. The candles thus obtained are bleached by arranging them vertically on trucks in metal gauze frames and leaving them for some days in the open air exposed to the action of the air, sunlight, and dew.

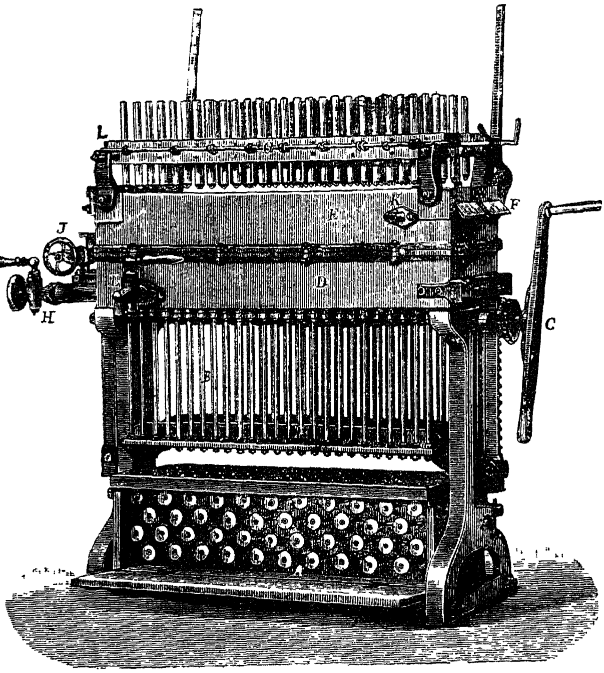


FIG. 276.

After this, the candles are washed, polished, and sawn off to a uniform length in a machine of the Binet type (Fig. 277). The candles are first dipped in a bath, *V*, containing soapy water or a dilute solution of soda, and are then placed in the grooves of the wheel, M, the head being against the left-hand edge, while the bases are cut off by a small circular saw, *n*; the fragments drop on to the frame, *X*, and so into the box beneath. The candles fall into the grooves of the travelling endless plane, *TM′*, and are rubbed and polished by a brush, *B*, moved excentrically from *V′*; when they reach *M′* they fall into the trough, *E*. The finished candles are stamped auto-

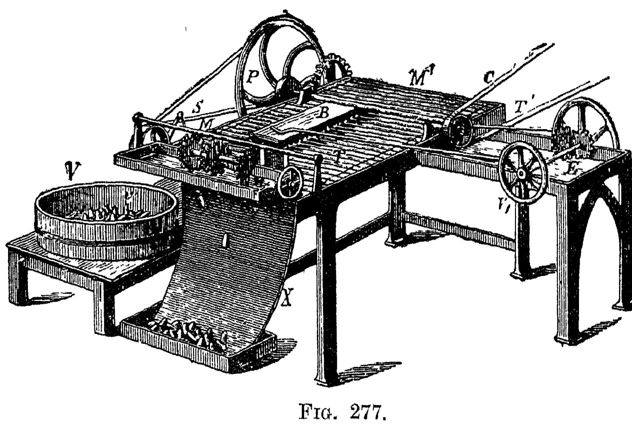


FIG. 277.

matically with the trade mark and are then tied and wrapped up in packets of 12 or 24 (or ½ or 1 kilo) and placed in wooden boxes for transport.

Some factories make lighter, perforated candles and some coloured candles or mixed candles containing wax or paraffin. To remove the semitransparency of *paraffin candles* and so make them resemble those of stearine, about 5 per cent. of stearine and 5 per cent. of paraffin oil are added. The same effect may be obtained with a small quantity of β-naphthol (Ger. Pat. 165,503) or any other substance which dissolves the paraffin in the hot and deposits it in the cold in a finely divided state (*e.g.* solid fatty acids, amides, phenols, ketones, &c.).

STATISTICS. The value of the stearine candles exported from England was £346,400 in 1892, £400,000 in 1900, £495,860 in 1909, and £485,220 in 1910, the output in 1907 being 10,000 tons, of the value of £1,640,000. France exported 25,120 quintals of stearine candles, worth £196,000, in 1890, and 43,300 quintals, of the value of £180,000, in 1900. In 1909 Germany imported 2200 quintals of candles and exported 7880. The United States exported 1500 tons (£58,200) in 1910 and 1450 tons (£55,600) in 1911.

In 1903 there were about 250 factories in Italy for candle-making only, the total horse-power of the engines being 185 and the number of operatives 1430; there were, in addition, 188 factories for both candles and soap, employing 2700 workpeople and using 830 h.p. In 1876 there were but 10 factories with 550 operatives.

In 1875–1879 Italy imported on an average 6350 quintals of candles per annum and exported 650 quintals, whilst in 1900–1904 the imports averaged 551 and the exports 1420 quintals annually. In 1905 the imports were 869 quintals, worth £4172, and the exports 614 quintals, of the value of £2948; in 1910 the exports fell to 582 (£2920) and the imports to 380 quintals (£1900).

MANUFACTURE OF SOAP[1]

Theoretically soaps include all metallic salts of the higher fatty acids, but practically the name is given only to salts of oleic, stearic, and palmitic acids, and, in general, of the fatty acids contained in natural oils and fats. Importance attaches mainly to the sodium soaps and, to a less extent, to those of potassium and ammonium. It was at one time thought that soaps were composed largely of *margaric acid*, but it has been shown that this acid does not occur in natural fats, the confusion arising from the fact that a mixture of palmitic and stearic acids was obtained with a melting-point identical with that of synthetic margaric acid (*see* p. 290).

Almost in its entirety soap is used for washing and for cleansing and removing grease from textile fibres, sweaty garments, and the greasy, dirty

[1] History of Soap. Soap was not known to the ancient Hebrews and Phœnicians or to the Greeks of the time of Homer, who washed their garments with the ashes of plants and water, and by mechanical rubbing. Some races used the juices of certain plants, and later it was discovered that when ashes were heated with lime they gave rise to *natron*, which was much more effective than the ashes themselves. Yet the writers of the Bible, who are certainly not conscientious and exact historians, several times mention soap and quote the following supposed phrase of the prophet Jeremiah (who would have lived several centuries before the Christian era): "Though thou wash thee with nitre [natron] and take thee much soap, yet thine iniquity is marked before me." Seneca and Pliny mention soap in their writings and attribute its discovery to the Gauls, who prepared it from the ashes of plants and goats' fat and used it as a hair-wash and for medicinal purposes (lead plaster). It is said that Galen (second century of the Christian era) proposed the use of soap for washing. In the excavations of Pompeii has been found a complete soap factory with utensils and saponified material. Marseilles did a large trade in soap as early as the ninth century, but in the eleventh century it had a serious rival for the premier position in Savona. In the fifteenth century the industry flourished at Venice, and in the seventeenth at Genoa, which, together with Savona, Marseilles, and Alicante, enjoyed a monopoly in soap-making. In England the industry began to develop after 1650, and in Germany it assumed considerable importance after Chevreul's investigations on fats (1810–1823). With the development of the soda industry and increase of the trade in palm oil and coco-nut oil, the conditions in Germany and, to some extent, in other countries favoured extension of soap-making. At the present time Marseilles, although partly surpassed by the large English factories, still preserves its early fame, which, however, the Italian factories have lost. But several times in the past the renown of Marseilles has been dimmed owing to the custom, even in the early days, of adulterating soap and of loading certain qualities of white soap with enormous quantities of water. This explains why, for several generations, the public preferred mottled soaps, which could not then be adulterated. It explains also the various laws promulgated in France against dishonest soap-makers, who in 1790 provoked a general protest of all the population and a petition to the deputies of the States General from all the laundresses of Marseilles to protest "*against the adulteration of white soap and against the malefactors who adulterate it to increase its weight.*" It does not appear that things have changed greatly after the lapse of 120 years, for, since the introduction of palm oil and coco-nut oil in 1850, the consumer has always paid for a considerable amount of water in place of soap.

epidermis of the human body, but it is sometimes employed as a subsidiary dressing in certain industrial operations, *e.g.* in the dyeing of silk and cotton, &c.

The theory of the saponification of fats has already been discussed on p. 377, and we shall here consider the *cleansing action* of soaps. It is well known that the quantity of fat or grease that a soap is able to remove from a dirty garment is greater by far than corresponds with the amount of alkali liberated on dissolving the soap in water.

Being formed from weak acids, soap in dilute aqueous solution is undoubtedly partly dissociated into caustic alkali and either acid soaps in the cold or fatty acids in the hot. This can readily be shown by the opalescence of the dilute aqueous solutions and by the violet colour imparted to phenolphthalein by a perfectly neutral (*i.e.* not yet dissociated) alcoholic solution or highly concentrated aqueous solution of soap, after pouring into a large quantity of water. If, then, part of the grease can be rendered soluble by the saponifying action of the alkali gradually liberated from the soap, another part is certainly carried away mechanically by the *emulsifying action* of the soap itself and of its fatty acids ; this action is accompanied by the abundant production of lather, which, together with the water, incorporates and removes all the grease with which it comes into contact. It is for this purpose—the formation of lather and emulsification of the grease—that rubbing is necessary in the washing of a garment with soapy water. A mere solution of caustic soda, even in excess, does not produce a detergent effect equal to that of soap.

As regards the molecular condition of soap in its concentrated, non-dissociated solutions, it appears demonstrated that it there exists in a colloidal condition, since an increase in the concentration is not accompanied by rise in the boiling-point, which approximates to that of water, while the electrical conductivity is minimal. But, according to McBain and Taylor (1910), in highly concentrated solutions soap is apparently not a colloid, as it conducts the electric current.

The solubility in water of almost all soaps is diminished rapidly to the point of complete separation by the addition of soluble salts which do not decompose the soap, *e.g.* NaCl, KCl, Na_2SO_4, NH_4Cl, Na_2CO_3, and even NaOH, &c., this action being due to a change in the density of the solution and in its degree of dissociation. This phenomenon is the basis of the *salting-out* or *graining* of soap during its manufacture, but it must be noted that if the fats or fatty acids used in the making of the soap contain *hydroxy-acids*, these are almost entirely lost, as they are not separated as insoluble soaps by salting out, and mostly pass into the spent ley. Hence account is now taken of the proportion of fatty hydroxy-acids (less soluble in benzine than ordinary fats or fatty acids) present in fatty materials.

Sodium soaps are more stable than those of potassium or ammonium, since sodium salts *partly* displace potassium or ammonium from their soaps with formation of sodium soaps.

Alkali soaps are precipitated by the soluble salts of the alkaline earths and heavy metals in the form of insoluble metallic soaps. Strong acids separate the weaker fatty acids from soaps.

The alkaline soaps are usually soluble in alcohol and insoluble in ether, benzine, or benzene. Evaporation of the alcoholic solution yields a *transparent soap*.

Saponification of fats is accompanied by increase in weight, each molecule of glyceride that decomposes fixing 3 molecules of alkali or water. A fat containing a mixture of glycerides with a mean molecular weight of 880, in reacting with 120 of NaOH (3 mols. or about 13·6 NaOH per 100 of fat), gives 92 of glycerine and 908 of water-free soap. So that theoretically 100 kilos of fat can produce about 10·5 kilos of glycerine and 102 of soap ; in practice about 1·5 to 2 kilos of glycerine are lost, while 140 to 160 kilos of soap, containing a considerable amount of water, are obtained. Potash soaps are *softer* than those of soda, and soaps of liquid fatty acids *softer* than those of solid fatty acids.

Soap may be made either from the fatty acids obtained from fats by the methods described above, or from the fats themselves. In the former case the saponification is carried out mainly by sodium carbonate, and is completed (since with the carbonate it proceeds only to the extent of about 90 per cent.) by caustic soda. But in the latter case concentrated solutions of caustic soda in the hot are employed; the carbonate is, indeed, unable to resolve glycerides, and that amount of it which always occurs in the caustic alkali is lost during the subsequent operations of salting-out, &c.

Mention has already been made (*see* p. 379) of the process of decomposing fats in an autoclave by means of ammonia and sodium chloride, which was studied by Leuchs (1859), Witelw (1876), Buisine (1883), and Polony (1882), and improved by Garelli, Barbé, and de Paoli (Ger. Pat. 209,537, 1906). This process leads directly to the sodium soap with formation of ammonium chloride, from which the ammonia may be recovered in the usual way, and, according to the above patent, gradual decomposition of the ammonia by means of steam results in a considerable separation of the *solid fatty acids* from the liquid ones, the ammonia soaps of the former being the first to decompose. Such separation can be effected also by cold water, which dissolves the ammonia soaps of the liquid fatty acids (oleates) almost exclusively.

In the manufacture of soaps from fats or oils, various stages are to be distinguished: (1) mixing or pasting of the fat with the alkaline lye; (2) mixing in the hot to form the soap and separate it partially from the excess of water; (3) *salting-out* (or "graining" or "cutting the pan") to render the soap insoluble and separate it from the lye, which thus collects under the layer of soap; (4) *boiling* to saponify the last traces of fat, to eliminate the scum and the excess of water still remaining in the soap and to collect the latter into a perfectly homogeneous, curdy mass; (5) the soap is often subjected to a *finishing* process, that is, a final treatment with dilute alkali hydroxide or carbonate solution, in order to separate the more thoroughly the residual impurities (aluminium or iron soaps) and so avoid a partial mottling, and to give to the soap, first, the quantity of water necessary to the particular type, and, secondly, a still more homogeneous appearance.[1]

A well-finished soap contains 35 to 40 per cent. of water and only 0·20 to 0·36 per cent. of salt and free alkali together. When excess of free caustic soda remains in the soap, considerable *efflorescence,* due to formation of sodium carbonate by the carbon dioxide in the air, occurs at the surface during the subsequent drying. In order to avoid such a serious inconvenience, it is necessary to treat repeatedly with sodium carbonate solutions, because, even if a little of the latter is left in the soap, only a slight powder forms at the surface on drying and this can be readily eliminated. In some cases, a small proportion of a non-saponifiable fat (*e.g.* wool fat) or even of a dense mineral oil is added to the soap, the caustic soda being thereby preserved from direct contact with the air.

At one time the *coppers* used for soap-making were largely made of masonry, but nowadays they are almost universally of iron and are heated either by fire or by direct or indirect steam, as is shown in Figs. 278, 278A, 279, 279A. Small coppers hold 10 to 50 hectols. and large ones 100 to 400.

For every 100 kilos of fat to be saponified, a copper-volume of 500 litres is taken.

In most soap-works the mixing is done by wooden blades worked by hand, although coppers are made fitted with stirrers of various forms.

The saponification of 100 kilos of fat or oil requires theoretically about 136 kilos of NaOH, but practically rather more than this amount is used. *Tallow soap* is made in the

[1] *Finishing* is best effected when the soap contains a certain proportion of water, namely, 10 mols. of water (40·5 per cent.) per 1 mol. of sodium oleate, or 16 mols (48·5 per cent.) per mol. of sodium stearate. If the soap is more concentrated than this, it remains too viscous and opposes too great a resistance to the precipitation of the impurities and of the drops of saline and caustic solutions; but if, in the finishing, the necessary quantity of water is restored (by adjusting the *concentration* of the lye), a small part of the soap dissolves, the mass becomes more liquid and, on standing, the impurities are able to fall to the bottom the more readily. Soaps which are too insoluble in the salt solution or caustic lye (colza, sesamé, linseed, poppy-seed, &c.) can be finished only when mixed with readily soluble soaps (coco-nut, castor, &c.). On the other hand, it is necessary to prevent the soap taking up too much water, for, if this happens, it pastes together and adheres to the sides of the boiler, does not transmit heat readily to the interior and hence boils with difficulty, is not easily finished and becomes uneven. Agitation of the mass and the consequent inclusion of a considerable amount of air are to be avoided, the finishing being thereby retarded. When the finishing is complete and the mass has been allowed to stand, a slight frothy layer is observed at the surface and then comes the thick layer of pure, homogeneous soap, well separated from the lye; but above this is a small, irregular, and gelatinous layer composed of more soluble soaps (of hydroxy-acids) of calcium, magnesium, and iron, and of certain other impurities insoluble in the lye (colouring-matters, coagulated proteins, &c.), and it is this mass which forms the refuse.

following manner: The tallow is mixed and gently heated in the copper with about one-fourth of the necessary amount of caustic soda in the form of a solution of 10° Bé. First of all an emulsion is formed and then saponification gradually proceeds, the mass beginning to become homogeneous and the volume increasing slightly. When a little is removed on the blade, it forms a jelly which does not separate the lye, and the soap-boiler judges

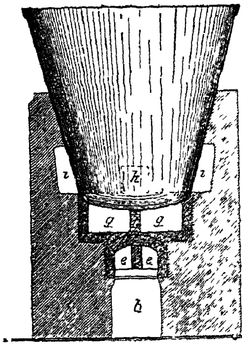


FIG. 278.

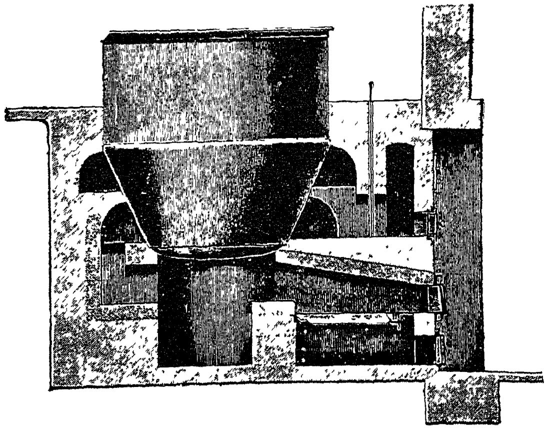


FIG. 278A.

of the fixation of the alkali by observing when the caustic taste of the alkali disappears. Much of the fat remains unsaponified, so that a hot caustic soda solution of 12° to 14° Bé. is gradually added until the stirred, boiling mass thickens, becomes clear and homogeneous, and falls from the spatula in transparent ribbons. At this stage, in order to judge if the alkali has been added in the proper proportion, a little of the soap is poured on to a glass plate; if a solid white edge first forms round the drop of soap, while the interior of the

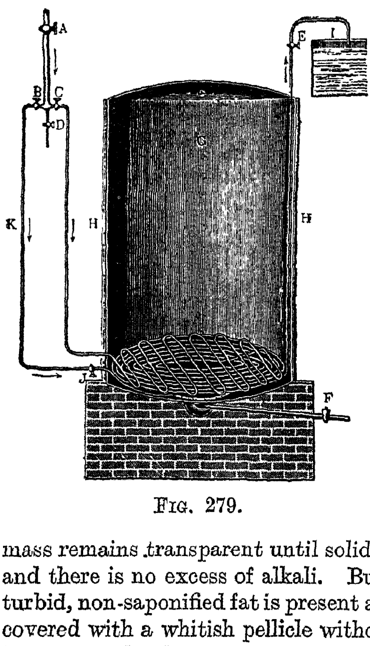


FIG. 279.

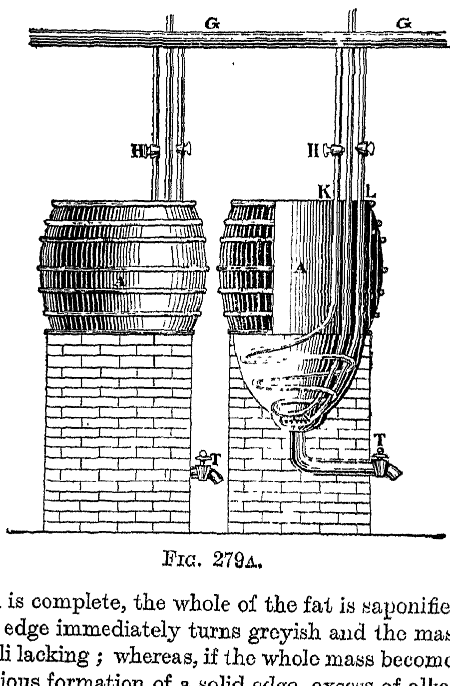


FIG. 279A.

mass remains transparent until solidification is complete, the whole of the fat is saponified and there is no excess of alkali. But if the edge immediately turns greyish and the mass turbid, non-saponified fat is present and alkali lacking; whereas, if the whole mass becomes covered with a whitish pellicle without previous formation of a solid edge, excess of alkali is present, this being corrected by adding a little fused tallow to the mass in the copper. Thus treated, the gluey paste, which has a slightly caustic taste, is boiled more strongly until it loses sufficient water to form a homogeneous ropy paste on the mixing-blade.

At this stage the separation of the soap from the liquid is induced by the gradual addition of salt either in the solid state (4 to 8 per cent. of the weight of fat) or in concentrated solution (20° to 22° Bé.). The first addition of salt renders the mass more fluid, while successive additions cause separation of the soap, which finally floats on the lye, the latter being drawn off after some hours by means of either a tap or siphon. When hard water is used, a little sodium carbonate is always added to the salt.

The residual lye should have, not a caustic but a brackish and somewhat sweet taste owing to the glycerine present, and its density should be at least 7° to 8° Bé. (for soaps from coco-nut, palm-kernel, oxidised oils, &c., 16° to 24° Bé.). If too little salt has been added, the lye will retain dissolved soap, and the separation of the latter will not be sharp, since between it and the lye will be formed a third layer consisting of an irregular, gelatinous mass which increases the waste and diminishes the yield. With too much salt, the soapy mass separates rapidly and in large clots which retain the lye. But if the operation has been properly carried out, the soap adheres to the mixer in soft flocculent masses which, when squeezed between the fingers, are moderately stiff, do not exude liquid and give a hard and dry, not a sticky, flake.

When treated repeatedly with salt solution, some soaps lose part of their combined alkali owing to the readiness with which they dissociate; in such cases a little caustic soda is added to the salt.

The soap is then subjected to the *boiling* process (in some cases this is preceded by a further heating with weak alkali of 4° to 6° Bé. and a little salt, the subnatant lye being decanted after a time). This consists in covering the copper, boiling vigorously, and, if necessary, stirring to prevent the frothing mass from overflowing. By this means the small quantity of residual lye is concentrated and hence separates more easily, while the soap gradually becomes denser owing to the loss of nearly the whole of the water (only 15 to 35 per cent. being left). The bubbles at the surface gradually increase in size and then disappear completely, while large bubbles of steam form at the bottom of the copper, force their way noisily through the mass and produce large puffs at the surface. The heat (fire or steam) is then very soon stopped. A little of the soap pressed between the thumb and the palm of the hand then forms a dry, soft, waxy paste, but does not stick.

The soap could next be moulded, but it is often subjected to a *finishing* process (*see above*), dilute caustic soda (3° to 6° Bé., or hot water alone if the soap has been treated originally with excess of alkali, or very dilute sodium carbonate) being gradually added to the soap in the boiler, the mass being heated and gently stirred until it becomes more liquid, less granular and perfectly uniform. The copper is next covered and left for a day, the soap being then transferred to the moulds or cooling frames. To obtain white soap, an addition of 0·1 to 0·3 per cent. of sodium hydrosulphite is sometimes made to the mass before discharging.

As a rule, soaps are made not from pure tallow, but from mixtures of various fats and oils, *e.g.* palm oil, olive oil, oleine, &c.; in such cases the concentration of the caustic soda must be varied, olive oil soap, for example, requiring lye of 25° to 28° Bé., which sometimes escapes salting-out.

At one time *Marseilles soaps* were prepared from olive oil alone, very dilute lye being first used and then more and more concentrated ones. But nowadays cotton-seed, arachis, coco-nut, palm-kernel oils, &c., are generally added, the processes employed, whether for white or for Marseilles mottled soap, being those used for other soaps.

SOAPS FROM FATTY ACIDS or **OLEINE.** Oleine, elaine, or commercial oleic acid forms a more or less dense liquid with a colour varying from pale yellow to dark brown. Less highly coloured is the oleine obtained by saponification of pure fats in autoclaves and separation from the stearine by pressing (*oleine of saponification*) or by enzymic or catalytic decomposition (*catalytic oleine*), whilst that obtained from impure fats (bone fat, &c.) or by means of sulphuric acid is generally darker and is separated after distillation of the fatty acids (*distillation oleine*). If an oleine contains more than 3 per cent. of non-saponifiable substances, it is certainly distillation oleine (1 to 9 per cent.), but a less content than this does not necessarily indicate oleine of saponification since the modern methods of exact distillation yield oleines almost free from non-saponifiable matter.

Oleine always contains small quantities of neutral fats and, more especially, of solid fatty acids (5 to 20 per cent. palmitic, stearic, &c.), but its iodine number should be between

75 and 85, and its acid number at least 179 (about 90 per cent. of fatty acids, expressed as oleic acid).

Oleine of saponification is now sold at a rather lower price than tallow, and distillation oleine at a still lower price (48*s.* to 56*s.* per quintal). Besides for soap-making it is used for treating wool which is to be carded or combed.

Pure oleic acid and its properties have already been considered on p. 298.

The manufacture of soap from fatty acids (*see* p. 406 *et seq.*), although it gives no glycerine, is economical in various ways; thus, it allows of a more rapid saponification with a diminished consumption of fuel and renders possible the use of sodium carbonate, which is cheaper than caustic soda.

100 kilos of oleine would require about 19 kilos of sodium carbonate (instead of 13·5 of caustic soda), but in practice only about 90 per cent. of this amount is used, the saponification being completed with caustic soda in order to transform the small amount of neutral fat present in the commercial oleine. A hot solution (about 30 per cent.) of the whole of the sodium carbonate is prepared in a wide, shallow copper, the oleine being then added gradually in a thin stream, the mass being mixed and heated by a jet of direct steam so as to liberate the carbon dioxide and prevent the froth from overflowing; the latter end is best attained by adding a little salt to the soda solution at the beginning or by the passage of a current of air. The caustic soda solution (15° to 18° Bé.) is then introduced and the whole heated, salted-out and boiled, as already described for tallow soap. Pure oleine soap is at first rather soft, but it gradually dries, hardens, and becomes of a paler yellowish brown colour than the fresh soap.

When soap is made from oleine and fats together, the latter are first saponified and the oleine added subsequently.

RESIN SOAPS are now made in large quantities and by almost all soap manufacturers. **Colophony** (*see* Part III) contains acids which behave like the fatty acids and yield similar soaps, which lather well with water and, when mixed with ordinary fat soaps, diminish the price considerably, as colophony costs only 14*s.* to 28*s.* per quintal.

The saponification of the resin is effected with a rather strong lye (to avoid excessive frothing). It is necessary to employ pure fats and pure resin (with the saponification number 160 to 180), and when saponification is complete, the soap must be well "finished" in order to avoid excess of alkali, which would cause *efflorescence* (also avoidable by the addition of a little sodium silicate at the end of the manufacture).

The resin may be introduced as a powder directly into the fused fat, but it is more generally added after the fats have been saponified and the soap salted out and separated from the lye. The concentrated caustic soda (100 kilos at 20° Bé. or 90 kilos at 25° Bé. per 100 kilos of resin) is then added and the resin gradually disintegrated by heating and stirring. Boiling is continued until the froth almost disappears and the soapy mass separates well from the lye below and exhibits the proper consistency when pressed between the fingers. After the lye has been removed, the soap is finished with a little boiling water, then left for 12 to 24 hours, and finally solidified in the ordinary frames or moulds.

Good resin soaps should not contain more than 40 per cent. of resin, but in some cases they show as much as 100 per cent. (compared with the fat), and it is a question whether resin soaps should be regarded as adulterated; to this view the manufacturers object, for obvious reasons. Although attempts have been made at various congresses to fix limits (10, 20, or 30 per cent.) to the proportion of resin allowable, none of these are regarded. The case would be met by stamping the resin-content on every cake of soap, as there could then be no question of adulteration or fraud.

Some soaps are not separated from the lye, or grained or finished, but are left mixed with the lye and the glycerine; the fats employed must here be pure, since otherwise the impurities would colour the soap. Coco-nut oil and palm-kernel oil are more especially used, as they have the property of becoming incorporated or remaining dissolved in a large excess of alkali or salt and of forming hard soaps with even large proportions of water (200 to 300 per cent.). They are made by either the hot or the cold process, and are generally cheap soaps, as they can be resined and charged, not only with large quantities of water, but also with salt, silicate, talc, flour, &c. Solutions of salt or caustic soda (20° Bé.), even in excess, facilitate hardening, whilst potassium carbonate produces a certain softness and lustre. The silicate and salt are mixed with hot caustic soda and are

added finally to the soap at 90° to 95°. The method of procedure is that generally employed: the fat is added to part of the caustic or carbonate solution with which it is stirred and heated to boiling; the rest of the alkali is then introduced and finally the salt or silicate solution in small portions; the mass is mixed, left in the covered copper overnight, when it falls to a temperature of 75°, then skimmed and cooled in the frames.[1]

When these soaps are prepared in the cold, the palm-kernel or coco-nut oil is mixed with the theoretical quantity of concentrated caustic lye (for coco-nut oil, 50 per cent. of lye at 38° Bé.), which saponifies these and other fats (tallow, lard, cotton-seed oil, arachis oil, resin, &c.), even in the cold, with spontaneous rise of temperature; they are commonly loaded with silicate, talc, salt, &c.

MOTTLED SOAPS. Until 30 to 40 years ago, mottled soap of the Marseilles type was made with olive oil, the mottling being produced by adding to the soap, either before or after graining, ferrous sulphate, ferric oxide, ultramarine, &c. (0·2 to 0·6 per cent. of the weight of fat), discharging into the cooling frames at a temperature of 75° to 80° and allowing to cool slowly (4 to 6 days).

Mottling is satisfactory only when the soap does not contain more than 32·5 to 34 per cent. of water, and hence constitutes a safeguard to the consumer showing that he is not being cheated with soap overcharged with water. Olive oil soap can be well mottled if it does not contain more than the above quantities of water and colouring-matter, and not more than 2 per cent. of salt, since it is only under these conditions that it acquires just that fluidity which, at the solidifying temperature, offers a resistance to the minute coloured particles (iron, aluminium, and manganese soaps, and metallic hydroxides); the latter gradually group themselves into veins, whilst the drops of lye and soluble salts fall to the bottom. If the quantity of water is raised, the equilibrium is displaced and the fluidity increased, so that the colouring-matters are deposited. But if other solid fats are used in conjunction with the olive oil, the required consistency can be obtained with as much as 50 per cent. of water. With coco-nut, palm-kernel, and palm oils, mottled soaps can be prepared containing 70 per cent. or even more of water, in addition to an increased amount of alkali. These soaps, however, should not contain more than 2 per cent. of sodium carbonate and less than 10 per cent. of dissolved salts; otherwise the soap will effloresce on drying, provided that it is sufficiently stiff to permit of mottling.

A type of mottled soap which is often prepared with a yield of 180 to 200 per cent. is that from almost equal quantities of sulphocarbon olive oil and coco-nut or palm oil. In this case the manufacture of the olive oil soap is carried out separately as far as the stage where it is separated from the lye, so as to remove the impurities: it is then introduced into the pan where the coco-nut oil has been saponified in the hot with caustic soda of about 20° Bé., together with some 13 per cent. of sodium carbonate dissolved in water. Unger (1869) found that, in order to prevent coco-nut or palm oil soap from efflorescing on drying, it should not contain more than 43 per cent. of sodium carbonate, calculated on the weight of coco-nut oil (*i.e.* 1 mol. of sodium carbonate per 4 mols. of pure coco-nut soap). After mixing, the two soaps are boiled and 4 to 5 per cent. (on the total fat) of sodium chloride solution of 24° Bé. gradually added; the heating is continued until the paste boils readily without adhering to the sides of the copper, and the steam evolved produces, at the surface of the soap, veinings and crevices in the form

[1] High yields are given by the following mixtures

Yield	Coco-nut oil	Crude palm-kernel oil	Palm oil	Tallow	Resin	Caustic soda (26° Bé.)	Potassium carbonate 25°–30° Bé.	Salt 20°–22° Bé	Salt 8°–10° Bé.	Sodium silicate
	kilos	kilos								
About 250 %	90	[or 90]	—	10	—	60	65	40	—	—
,, 300 %	—	100	—	—	—	60	100	65	—	—
,, 300 % (resined)	50	40	20	—	15	60	65	65	—	—
,, 400 %	100	[or 100]	—	—	—	60	100	100	50	30
,, 800 %	100	[or 100]	—	—	—	80	260 (20° Bé.)	300	60	—
,, 1000 %	100	—	—	—	—	150–160 (22° Bé.)	—	—	—	800

of rosettes. The soap will then emit a hollow sound and will not form bubbles when struck with the stirrer, from which it falls in broad folds which become covered with a dry skin ; when placed on glass, it is quickly coated with a solid layer beneath which it remains fused, while between the fingers it does not pull out, but tends to solidify. It is important that it should not contain an excess of caustic soda (not more than 0·2 to 0·3 per cent. ; it is *best neutral*) as with finished soaps ; any excess may be eliminated by adding the calculated quantity of coco-nut oil or of hydrochloric acid, determined by titration. At this point the colouring-matter is well mixed in, the soap being then cooled to about 75° and poured into large solidifying frames (holding at least 10 quintals) so as to cause slow cooling (in winter these are wrapped round with cloths), and hence satisfactory mottling. These mottled soaps of high yield (up to 400 per cent.) bear the name of blue mottled or *Eschweg soaps*, and were largely used some years ago. Even now their consumption is considerable, as they have a higher detergent power than finished soaps owing to their richness in alkali carbonates ; they dry more rapidly than resin soaps and owing to their hardness they are preferred for laundry purposes, there being no waste even when the clothes are vigorously rubbed.

The formation of mottling in soaps probably obeys the laws holding in the solidification of alloys (*solid solutions*) and the figures given on pp. 412 and 642, and in Plate III. of vol. i of this work ("Inorganic Chemistry") represent well the impression produced by the mottling of soap.

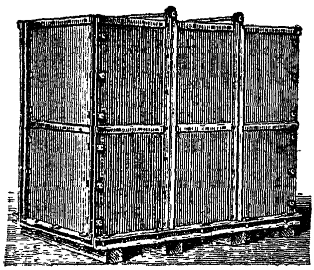


FIG. 280.

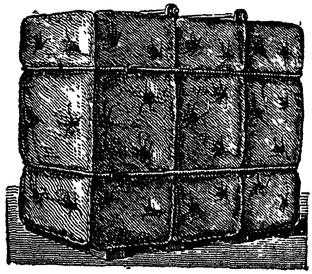


FIG. 281.

When *almond-mottling* is required, an iron rod 12 to 15 mm. in diameter is drawn vertically through the semi-solid soap in the solidifying frame, so as to make a kind of longitudinal cut ; similar cuts, parallel to the first, are then made throughout the whole mass at distances of 4 to 6 cm., and afterwards a similar series perpendicular to the others. When solidification is complete, the whole of the soap is traversed by dark markings in the shape of almonds arranged like the leaves on acacia twigs. Other mottlings are made either by machinery or by hand.

For Eschweg soaps mixtures of various fats are used, *e.g.* 20 to 25 per cent. of tallow, 25 to 30 per cent. of bone fat, 10 to 15 per cent. of cotton-seed oil, 20 to 40 per cent. of palm-kernel oil, and 20 to 30 per cent. of coco-nut oil. The yield is usually 205 to 215 per cent., although additions of silicate (10 to 12 per cent.) are sometimes made.

TRANSPARENT SOAPS were at one time obtained by dissolving ordinary soaps in alcohol, evaporating the latter and moulding the transparent residue. The amount of alcohol used was subsequently diminished by adding glycerine, and at the present time transparent or so-called glycerine soaps are made from mixtures of decolorised tallow with castor, linseed, and coco-nut oils, with addition of glycerine and also of 20 to 30 per cent. of saccharose or glucose, which enhances the transparency. To this mixture, melted in the copper, is added caustic lye at 30° to 36° Bé., the whole being mixed until a homogeneous emulsion is formed ; 2 to 5 per cent. of alcohol is then introduced, and the mass heated to 75°, cooled to 50°, and poured into the moulds. For some of these soaps as much as 40 per cent. of pale resin is employed.

SOFT SOAPS are usually potash soaps of linseed oil or oleine, while in summer cotton-seed, colza, sesamé, palm, or fish oil is also used.

Some of these soaps are transparent (plain or variegated), others opaque and white or yellowish. For every 100 kilos of fat, about 160 kilos of caustic potash of 24° Bé. are used, the yield being sometimes as much as 235 per cent. ; if caustic soda is partly

employed, a harder soap is obtained, but the yield is diminished. Also 10 to 15 per cent. of resin may be used or 10 to 15 per cent. of oil. In general these soaps contain carbonates.

The boiling is carried out in the usual way, and is continued until frothing ceases, and a small portion placed on glass remains clear for some time without forming a skin and, on cooling, becomes turbid at the edges and exhibits slight veinings of lye. If this test portion remains clear but presents no such veinings, lack of alkali is indicated.

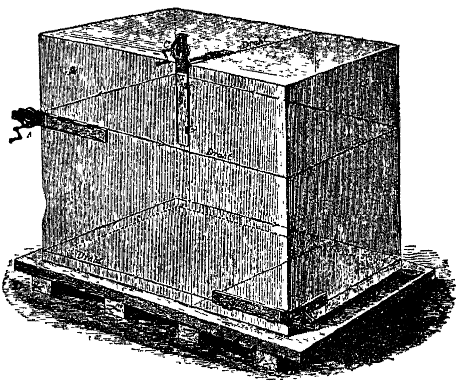


FIG. 282.

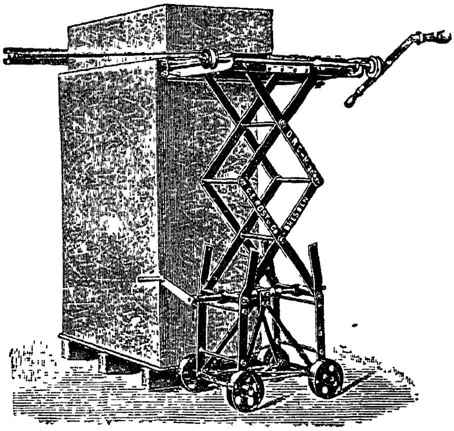


FIG. 283.

Many of the soft soaps now used contain white granules, produced by the addition of tallow or stearine, which crystallises out throughout the mass of soap during the cooling, the latter occupying 4 to 8 weeks; this change is known as *figging* and the yield of such soaps is often as high as 240 per cent.

The manufacture of soda soap from glycerides by means of lime and sodium carbonate (Krebitz process) has been described on p. 408.

Cooling and Solidification. The soap from the copper is cooled in large chests or *frames*, formerly of wood but now of iron, as was suggested by Krull in 1876 (Fig. 280). The sides of these are fixed by means of bolts and nuts and hence fit perfectly and are readily taken apart. In some cases, the frames are mounted on three wheels so as to be transportable. To prevent any impurities depositing in one place and so producing mottling, the pasty soap in the frame is stirred with wooden *crutches* until it begins to solidify; but, if slow solidification is required (for mottled soaps), the sides of the frame are covered with straw mattresses or wool, especially in winter (Fig. 281). The frames vary in capacity from 100 to 6000 kilos and, according to the amount and quality of the soap, the cooling lasts one or several weeks. The walls of the frame are then removed and the large block cut into smaller prismatic blocks by means of thin steel wires worked by a toothed-wheel winch, which is applied to various points of the block (Fig. 282). The small blocks are discharged on to a truck carrying a platform which can be raised (Fig. 283) and are then transferred to the *barring machine* (Fig. 284), where each block is placed between *A* and *B* and forced by means of the plate *A* and the toothed wheel, *R*, against the frame, *B*, fitted with adjustable crossed steel wires. The long bars thus

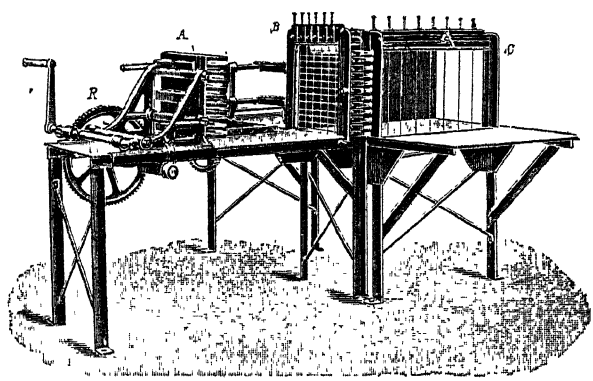


FIG. 284.

obtained between *B* and *C* are then pressed against the vertical wires of the frame, *C*, and thus cut into cakes of the required size. There are many such machines of different types, some fitted with fixed and others with universal frames.

During recent years a method has been devised of preparing cakes directly from the hot soap from the copper, without using the large cutting machines (*slabbers*); in this way much time is saved, waste and scraps are diminished in amount and the subsequent seasoning shortened. The hot soap is rapidly cooled and compressed in the Klumpp apparatus (Fig. 285), being first transferred to the jacketed reservoir, *L*, where it is kept liquid by means of hot water in the jacket. The plate, *c*, consisting of a double-walled box surrounded by cold water, has a movable base, *h*, resting on the piston of a hydraulic pump, *K*. The box, *c*, is filled with liquid soap and the wheel, *V*, turned so as to press on to the surface of the soap the large plate, *a*, which is kept horizontal by the four rods, *N*, of the press, while inside it cold water circulates.

When this plate is firmly fixed and the soap begins to solidify, a pressure of 50 atmos. is applied by means of the press, *K*, this pressure being increased to 250 atmos. when the soap is quite cold and solid. The ordinary cutting machines are then used to cut these slabs into marketable pieces, which lose little water even in the air.

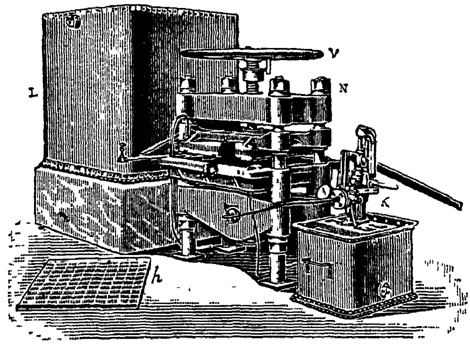


FIG. 285.

Seasoning or *drying* of the soap, to bring it to the degree of moistness required by the trade, is effected by keeping the cakes on frames in well-ventilated chambers for several weeks or even months. This slow drying is now generally replaced by drying in hot air, furnished cheaply by Perret furnaces, which burn waste coal or slack. The soap is spread out on gratings superposed on trucks, which are gradually introduced into a brickwork gallery; hot air traverses the gallery, entering at the opposite end at 50° to 60° and being discharged at 35° to 45°. The seasoning is complete in 3 to 6 days, but if the temperature is too high at first, or the drying too rapid, the soap softens and becomes deformed and crushed. To give the cakes a smooth surface, and so render efflorescence and cracking more difficult, as they issue from the dryer they are subjected to the action of a slight steam-jet, which melts them superficially.

STATISTICS. The largest and most up-to-date soap-factories of the present day are in the United States and England, next in importance being those of Germany and France.

Italy imports more than 220,000 quintals of fat (1904) for soap and candle-making. In 1894 there were 300 factories and an appreciable *exportation* (33,000 quintals of common soap and 1000 of perfumed soap) which in 1903 reached 40,680 quintals of common soap, sent to England and the United States, and 1230 of perfumed soap to India and Egypt. In 1909 the exports were 28,450 quintals of common soap, worth £74,000, and 2150 of perfumed sorts, worth £19,340; in 1910, 40,000 quintals of common soaps, valued at £104,200, and 1915 of perfumed (£17,240) were exported. The *importation* amounted to 16,369 quintals of ordinary and 964 of perfumed soap in 1903; to 19,000 quintals of common kinds from France and 1100 of perfumed from Germany, France, and England in 1904; to 23,230 quintals of common soap, valued at £48,400, 1120 of perfumed (£15,680), and 5300 quintals of *cart-grease* and *stiff fats*, consisting largely of lime soaps, resins, and mineral oils and valued at £2544, in 1905; 40,000 quintals of ordinary soap, costing £96,000, 1617 quintals of perfumed soap (£23,360), and 2500 quintals of cart- and engine-grease in 1910.

The total production of soap in Italy in 1905 was estimated at about 1,500,000 quintals.

France was at one time the greatest exporter of soap, 160,000 quintals of non-perfumed kinds being exported in 1890 and 268,000 (worth £440,000) in 1900; but at the present time England is far ahead. In 1898 France produced about 3,000,000 quintals of soap (one-fourth mottled), one-half of this in the Marseilles district; the total value was £5,600,000. The port of Marseilles receives annually 5,000,000 quintals of oily fruits

and seeds, and a similar quantity of crude oils and fats for extraction and refining (including mineral oils), the total yearly production of the Marseilles oil, soap, and stearine industries being nearly £40,000,000.

The province of Marseilles produced 500,000 quintals of mottled and 50,000 quintals of white soap in 1866 and 200,000 quintals of mottled and 1,400,000 of white soap in 1898.

In 1894 England exported 290,000 quintals of soap and in 1897 about 370,000; in 1900 the exports of soap were valued at £920,000, and those of stearine candles at £400,000; in 1907 the soap exported amounted to £1,480,000; and in 1909 to 650,000 quintals (112,000 being imported in that year). The English Sunlight Company alone has a capital of £14,000,000.

The production of soap in England in 1907 was as follows: soft soap, 49,900 tons; toilet soap, 70,400 tons; ordinary soap, 665,000 tons; and various other soaps, 24,200 tons, the total value being estimated at £7,055,000. The exportation of ordinary soap alone amounted to 119,540 tons in 1909 and 134,560 tons (£1,357,776) in 1910, in which year the imports were less than 20,000 tons.

The total production of soap in England is about 4,000,000 quintals per annum.

The United States produced soap to the value of £13,650,000 in 1904 and of £22,280,000 in 1909; the exports amounted to £789,000 in 1910 and £800,000 in 1911, and the imports to £165,000 in 1910 and £160,000 in 1911.

In 1903 Germany imported 7,740,000 quintals of oils and fats, and in 1905 about 9,000,000 quintals, of the value of £13,000,000, the exports in 1905 being 2,432,000 quintals, worth £2,920,000. Also, in 1905, 306,320 quintals (145,000 in 1903) of oleine, valued at £300,000, were imported.

In 1903 Germany exported 84,160 quintals of soap of all qualities, and in 1905 almost 99,000 quintals, worth £440,000, the imports in that year being 14,500 quintals, valued at £48,000; in 1905, the exports of soap were about £640,000.

In 1906 Japan imported soap to the value of £36,000, and in 1907 £52,000, half of the amount coming from Germany.

The Argentine Republic possesses 200 soap factories, representing a total capital of about £240,000, and giving an annual production valued at about £640,000; considerable quantities of perfumed and medicinal soaps are imported.

The value of soap[1] varies considerably with the quality, the degree of fineness, the

[1] **Analysis of Soap.** As a rule, the commercial value of a soap is determined from the quantity of combined fatty acids which it contains, and as the percentage of these varies with the degree of moistness, great care must be taken in sampling the soap. The cake is first weighed and the sample cut in such a way that the inner and outer portions are taken in the proper proportions; the sample is then cut up fine, rapidly mixed and immediately enclosed in a vessel with a ground stopper so that water may not be lost.

The analysis consists of some or all of the following determinations:

(1) *Water.* This estimation is not usually made, as it involves a long operation, while it is possible to calculate the proportion of water indirectly after all the other components have been determined. The direct estimation is made by weighing 5 to 10 grms. of the finely divided soap rapidly in a tared dish containing a small glass rod and filled to the extent of one-third with sand which has been previously calcined. The dish and its contents are heated first in an oven at 60° to 70°, the fused soap being carefully mixed with the sand until a skin of soap no longer forms at the surface; the temperature is then raised to 105° to 110°, at which it is maintained until constant weight is reached. The total loss in weight represents the water.

(2) *Unsaponified Fat.* The *dry* residue from the water estimation is introduced into a Soxhlet extractor (*see* p. 374) and extracted for a couple of hours on the water-bath with light petroleum in a tared flask; the solvent is subsequently distilled off and the extracted fat dried at 110° until of constant weight.

(3) *Fatty Acids, Free Alkali, Glycerine, and Resin* The residual matter in the Soxhlet apparatus (or the dry soap itself) is extracted with neutralised absolute alcohol, which dissolves the soap, glycerine, and *free caustic alkali;* the last of these is determined immediately by titrating the alcoholic solution with normal sulphuric acid in presence of phenolphthalein. The liquid is afterwards largely diluted with water, heated for a long time on the water-bath to remove all the alcohol, and treated with a measured volume, in excess, of normal sulphuric acid, the liquid being then heated in a beaker on a water-bath and on a sand-bath until the *clear* fatty acids (and the resin, if present) separate at the surface. After cooling, the solidified layer of acids is pierced with a rod and the liquid poured on to a tared filter in a stemless funnel, the fatty acids being then washed with hot water, and the whole brought on to the filter. The excess of free sulphuric acid in the whole of the wash-water is determined by titration with normal caustic potash This then gives the amount of sulphuric acid fixed by the alkali of the soap and hence also the *combined alkali* expressed as Na_2O. Evaporation of the liquid to dryness and extraction with absolute alcohol removes any *glycerine* present in the soap, this being weighed after evaporation of the alcohol. The fatty acids on the filter are treated with a couple of c c. of alcohol to remove any moisture and then with sufficient light petroleum to dissolve all these acids; the filtrate is evaporated in a tared dish, dried at 105° to constant weight and the residual *fatty acids* weighed To determine any *resin* which may be present in the fatty acids, part of the latter is weighed, dissolved in 20 c.c. of alcohol and, after addition of phenolphthalein, hydrolysed in the hot with a slight excess of alkali; after cooling, the liquid is made up to 110 c.c. with ether, treated with powdered silver nitrate and allowed to deposit the precipitated silver stearate, palmitate, and oleate. One-half of the filtered solution (containing soluble silver resinate) is treated with 20 c.c. of dilute

content of fatty acids, and the degree of purity. The ordinary soaps used in laundries and in the textile industries, which are made from sulphocarbon olive oil and contain 60 to 65 per cent. of fatty acids, cost 44*s*. to 48*s*. per quintal, according to the conditions of the market and the prices of prime materials (fats and oils). Soaps loaded with water and other substances may cost much less ; fine, perfumed soaps cost up to £4 to £8 per quintal.

GG. POLYHYDRIC ALDEHYDIC OR KETONIC ALCOHOLS

CARBOHYDRATES

(Sugars, Starch, Cellulose)

This group of substances might have been included in the preceding chapter, **FF**, where, in paragraphs **D** and **E**, certain very simple aldehydic and ketonic alcohols have been considered. But, partly owing to custom (since it has been the rule to include in the group of **Carbohydrates** only ketonic or aldehydic polyhydric alcohols with six [*monosaccharides*] or a multiple of six carbon atoms [*polysaccharides*] and containing hydrogen and oxygen in the proportion of 2 : 1, as in water), and partly because this group embraces all the sugars, which exhibit special characters very different from those of glycollic aldehyde (which should be the first member). So that even at the present time the carbohydrates are considered separately, although the brilliant researches of Emil Fischer, commenced in 1887, have extended this group to compounds with five, four, or three carbon atoms, on the one hand, and to monosaccharides with six, eight, or even nine carbon atoms on the other.

These monosaccharides bear the name of **Monoses** (*bioses, trioses, tetroses, pentoses, hexoses, heptoses, octoses, nonoses*, &c., according to the number of carbon atoms they contain), while the polysaccharides (formed by the condensation of two or more monose molecules) are called generally *polyoses* and, in particular, hexabioses, hexatrioses, &c., according as they are formed by the condensation of two, three, &c., hexose molecules.

A. MONOSES

All the monoses are aldehydic or ketonic polyhydric alcohols containing the characteristic grouping, $-\underset{\text{OH}}{\overset{\text{H}}{\text{C}}}-\underset{\text{O}}{\text{C}}-$, *i.e.* a hydroxyl group united with a carbon atom adjacent to a carbonyl (CO) group. When the carbonyl exists as an aldehydic group, $-\underset{\text{OH}}{\overset{\text{H}}{\text{C}}}-\underset{\text{O}}{\text{C}}\cdot\text{H}$, these monoses are called **Aldoses**, whilst

hydrochloric acid (1 : 2) and filtered, an aliquot part of the filtrate being evaporated in a tared capsule, dried at 100° and the residual *resin* weighed ; the weight of the resin is diminished by 0·00235 grm. for every 10 c.c. of ethereal solution of silver resinate, this being the amount of oleic acid removed by the ether. The true weight of the fatty acids, free from resin, can then be calculated.

(4) *Soda, Salt, Sulphates, Silicate, &c.* The residue from the Soxhlet apparatus, after separation of the fat and soap, is treated two or three times with 50 to 60 c.c. of hot water and the solution filtered, made up to a definite volume and divided into four parts : one of these is titrated with normal sulphuric acid, using phenolphthalein as indicator, to ascertain the *sodium carbonate ;* in a second portion, the *sodium chloride* is determined by titration with silver nitrate ; the third is precipitated with barium chloride and the weight of the barium sulphate and hence that of the *sodium sulphate* in the soap, determined. The fourth portion is treated with hydrochloric acid and the silica, thus separated from the silicate, weighed.

(5) *Ash and Mineral "Filling."* The ash obtained by burning a definite weight of pure soap is about 40 per cent. greater than the total alkali (expressed as Na_2O). If the proportion is much higher than is indicated by this relation, the excess represents mineral *filling*.

when it exists as a ketonic group, $-\underset{OH}{\overset{H}{\dot{C}}}-\underset{\ddot{O}}{C}-\overset{|}{\underset{|}{C}}-$, they are termed *ketoses*, so that we have *aldohexoses*, *ketohexoses*, &c.[1]

The monoses have the general properties of the aldehydes or ketones and hence form, on oxidation, the corresponding monobasic acids, *e.g.* *pentonic*, *hexonic acids*, &c. Since the aldoses contain a primary alcoholic group,

$$OH \cdot CH_2 \cdot [CH \cdot OH]_n \cdot C\begin{smallmatrix} \diagup O \\ \diagdown H \end{smallmatrix},$$

they can also be oxidised to dibasic acids containing the same number of carbon atoms, whilst when the ketoses are oxidised, the carbon atom chain is ruptured and acids with lower numbers of carbon atoms formed.

On reduction, both the aldoses and the ketoses take up two atoms of hydrogen, forming the corresponding alcohols; the hexoses give *hexitols* and the pentoses *pentitols*.

Like all aldehydes, they reduce ammoniacal silver solutions in the hot, giving silver mirrors.

When heated with alkali, they turn brown and then resinify.

They reduce alkaline copper solution (Fehling's solution) in the hot.

When heated with excess of phenylhydrazine dissolved in acetic acid, they yield yellow, crystalline *phenylosazones*, insoluble in water.[2]

In dealing with the hexoses later on, we shall see how the constitutions of the monoses in general are determined.

Of the various monoses, containing from 2 to 9 carbon atoms, only certain of the hexoses are *fermentable*, that is, give alcohol and carbon dioxide under the action of ferments or enzymes (*see* pp. 112 and 122). Of the hexoses, some ferment readily, others with difficulty, and others again not at all, in dependence on their stereochemical configurations and possibly on the asymmetric constitution of the enzymes. d-Glucose, d-mannose, and d-fructose ferment easily, and d-galactose with difficulty, whilst l-glucose and l-mannose do not ferment.

GENERAL METHODS OF FORMATION OF THE MONOSES:

(*a*) From the polyoses by *hydrolysis* with dilute acids, water being added and several molecules of hexose obtained:

$$C_{12}H_{22}O_{11} \text{ (saccharose)} + H_2O = 2C_6H_{12}O_6.$$

(*b*) By oxidation of the corresponding alcohols by nitric acid: *e.g.* **Arabitol**, $C_5H_{12}O_5$,

[1] The two classes of sugars, *aldoses* and *ketoses*, are distinguished by means of Romijn's reaction with a solution of iodine and borax, which *oxidises all the aldoses* (galactose, glucose, mannose, arabinose, xylose, rhamnose maltose, lactose), while it either does not oxidise the *ketoses* or oxidises them but slightly (sorbose, fructose; saccharose and raffinose are oxidised to a small extent).

[2] They form first *phenylhydrazones* (*see* p. 206):

$$\begin{array}{l} \quad | \\ H-C-OH \\ \quad | \\ \quad C=O \\ \quad | \end{array} + H_2N \cdot NH\,C_6H_5 = H_2O + \begin{array}{l} \quad | \\ H-C-OH \\ \quad | \\ \quad C=N \cdot NH \cdot C_6H_5; \\ \quad | \end{array}$$

these *phenylhydrazones* then react with two other molecules of phenylhydrazine, giving ammonia, aniline, and *phenylosazone*:

$$\begin{array}{l} \quad | \\ H-C-O-H \\ \quad | \\ \quad C=N \cdot NH \cdot C_6H_5 \\ \quad | \end{array} \begin{array}{l} NH_2\,NHC_6H_5 \\ + H_2N \cdot NHC_6H_5 \end{array} = NH_3 + \underset{\text{aniline}}{NH_2 \cdot C_6H_5} + H_2O + \begin{array}{l} | \\ C=N \cdot NHC_6H_5 \\ | \\ C=N \cdot NHC_6H_5 \\ | \end{array}$$

which is the characteristic group of the phenylosazones. The latter crystallise readily and in a pure state from a dilute pyridine solution. Reduction of the phenylosazones yields *osamines*, *e.g* *glucosamine*, $C_6H_{11}O_5\,NH_2$.

gives **Arabinose**, $C_5H_{10}O_5$ (pentose); *xylitol* (stereoisomeric with arabitol) gives xylose and **Mannitol**, $C_6H_{14}O_6$, mannose.

(*c*) Oxidation of glycerol gives dihydroxyacetone, $\mathrm{OH\cdot CH_2\cdot CO\cdot CH_2\cdot OH}$, which is a triose, its constitution being indicated by the fact that it forms a cyanohydrin, $\mathrm{OH\cdot CH_2\cdot C(OH)(CN)\cdot CH_2\cdot OH}$, the latter yielding *trihydroxyisobutyric acid*, $\mathrm{OH\cdot CH_2\cdot C(OH)(COOH)\cdot CH_2\cdot OH}$, and this, on reduction, isobutyric acid having a known constitution.

(*d*) By treating the bromo-derivatives of the aldehydes with baryta water. Thus monobromaldehyde gives **Glycollic Aldehyde**,

$$\mathrm{CH_2Br\cdot C}\Big\langle{}^{O}_{H} + \mathrm{H_2O = HBr + OH\cdot CH_2\cdot C}\Big\langle{}^{O}_{H},$$

which is the *simplest member of the sugar group* and does not give all the reactions of the sugars.

(*e*) With lime-water, formaldehyde undergoes *aldol condensation* (*see* p. 205), giving **Formose**,

$$6\,\mathrm{H\cdot C}\Big\langle{}^{O}_{H} = \mathrm{OH\cdot CH_2\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot C}\Big\langle{}^{O}_{H},$$

which is a syrupy mixture of compounds, $C_6H_{12}O_6$.

Under the influence of light and moisture, plants fix CO_2 and form starch $(C_6H_{10}O_5)_n$, which is a polyhexose, $6CO_2 + 6H_2O = C_6H_{12}O_6 + 6O_2$, the hexose then giving up water and yielding starch. According to Baeyer, the CO_2 gives first formaldehyde, then a hexose (monose), and finally starch (polyose).[1]

Also 2 mols. of glyceraldehyde (derived, *e.g.* from acrolein) undergo the aldol condensation and yield a hexose (termed *acrose*) which is a constituent of formose.

(*f*) It is possible to pass from one aldose to a higher one through the cyanohydrin, which is first hydrolysed to an acid with an extra carbon atom. Such an acid readily forms a *lactone* with the hydroxyl in the γ-position, and treatment of the lactone with sodium amalgam (addition of H_2) yields the higher aldehyde (aldose):

$$\mathrm{OH\cdot CH_2\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot C}\Big\langle{}^{O}_{H} \longrightarrow$$

$$\overset{1}{\mathrm{OH\cdot CH_2}}\cdot\overset{2}{\mathrm{CH(OH)}}\cdot\overset{3}{\mathrm{CH(OH)}}\cdot\underset{\gamma}{\overset{4}{\mathrm{CH(OH)}}}\cdot\underset{\beta}{\overset{5}{\mathrm{CH(OH)}}}\cdot\underset{\alpha}{\overset{6}{\mathrm{CH(OH)}}}\cdot\overset{7}{\mathrm{COOH}} \longrightarrow$$

$$\mathrm{OH\cdot CH_2\cdot CH(OH)\cdot CH(OH)\cdot}\underbrace{\mathrm{\overset{\gamma}{C}H\cdot CH(OH)\cdot CH(OH)\cdot CO}}_{\mathrm{O}} + \mathrm{H_4} \longrightarrow$$

$$\underset{\text{Heptose}}{\mathrm{OH\cdot CH_2\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot C}}\Big\langle{}^{O}_{H}.$$

By the same ketonic (lactonic) synthesis, the *heptose* can be converted into *octose* and *nonose*.

[1] It was shown by Butlerow that formaldehyde—and later by E. Fischer that glyceraldehyde—can, under certain conditions and in the presence of bases (baryta), give rise to sugar (α-acrose). In 1905 H. and A. Euler found that under no conditions do other alkali hydroxides give an appreciable amount of sugar, whilst with dilute solutions of sodium carbonate or, better with calcium carbonate or lead hydroxide at 100°, first glycollic aldehyde and glyceric aldehyde are formed and finally a *keto-arabinose*, the phenylosazone of which melts at 159° to 161°. The conditions for the production of hexoses from formaldehyde are not yet defined, but O. Loew stated that, with milk of lime, he obtained *formose*, which is a mixture containing *i-fructose* (α-*acrose*).

D. Berthelot and H. Gaudechon (1910) found that the action of ultra-violet rays on 10 per cent. solutions of various sugars at a temperature of 80° to 90° leads to the rapid formation of the following quantities of gas:

	CO	CH_4	H_2	CO_2
Levulose (ketose)	83	8	9	15
Glucose (aldose)	12	12	76	22
Maltose (gives 2 mols glucose)	12	11	77	21
Saccharose (gives glucose and levulose)	45	8	47	16

They found also that prolonged action of ultra-violet rays on a mixture of CO_2 and H_2 yields a small quantity of CO and of formaldehyde.

These facts tend to confirm J. Stoklasa's observations (1906–1910) on the formation of hydrogen as final

TETROSES, $C_4H_8O_4$, and PENTOSES, $C_5H_{10}O_5$

Just as the hexoses can be converted into pentoses, the latter can give rise to **TETROSES**. For instance, *d-*, *l-*, and *i-erythrose* are obtained by oxidising d-arabonic acid, d-arabinosoxime, and natural *i-erythritol* respectively with hydrogen peroxide:

$$OH\cdot CH_2\cdot [CH\cdot OH]_3\cdot COOH + O = H_2O + CO_2 + \underset{\text{Tetrose}}{OH\cdot CH_2\cdot [CH\cdot OH]_2\cdot CHO}$$

The tetroses are also obtained by oxidising (with H_2O_2) the calcium salts of pentonic acids in presence of ferric acetate, which acts as an oxidising catalyst.

The pentoses (**Arabinose, Xylose,** &c.) occur abundantly as **Pentapolyoses** or **Pentosans** (**Araban, Xylan**) in many vegetable organisms (straw, wood, maize husks, &c.), from which they are obtained by simple boiling with dilute acids.[1] Pentoses do not ferment.

product of the degradation of carbohydrates by the action of *glycolytic enzymes*, which have an important function in the assimilation of carbon dioxide in the chlorophyll cells, and also to render valid Stoklasa's hypothesis (1907) that the formaldehyde necessary to the formation of carbohydrates by the simple polymerisation assumed by Baeyer can result from the reaction, $2CO_2 + 2H_2 = O_2 + 2H\cdot CHO$. Stoklasa and Zdobnický (1910) have obtained inactive sugars and aldehyde by the action of ultra-violet rays on carbon dioxide and hydrogen in the nascent state in presence of caustic potash (with initial formation of potassium bicarbonate, which, in the nascent state and with nascent hydrogen, generates the sugar) and have disproved the view held by Fischer (1888–1889), Loew (1888–1889), Neuberg (1902), and Euler (1906) that, in the synthesis of sugars from formaldehyde, pentoses are formed; the sugars they obtained are not asymmetric and are hence not fermented by ordinary alcoholic ferments. According to Stoklasa, the function of the *chlorophyll* in plants is to absorb the ultra-violet rays of sunlight. From the aqueous distillate of the leaves of various plants, F. Hartwig and T. Curtius (1910) have separated (by means of m-nitrobenzhydrazide, *α · β-hexylenealdehyde*, $CH_3\cdot CH_2\cdot CH_2\cdot CH : CH\cdot C\langle^{O}_{H}$, the hydrazone of which melts at 167°.

[1] By the term **Pentosans** are meant those polysaccharides which are related to the pentoses in the same way as are starch, inulin, &c., to the hexoses, and which give pentoses and also hexoses on hydrolysis. From starch they are distinguished by their lævo-rotation. From plants the pentosans are extracted by means of dilute alkali according to the method given by Tollens, Stone, and Schulze (1888–1901) the finely divided vegetable matter is treated twice, for some hours at the ordinary temperature, with seven times its weight of 2 per cent. ammonia solution to eliminate in the soluble state part of the proteins, salts, &c., and to remove the more soluble part of the hemicellulose (this would give little pentose on subsequent hydrolysis). After the dark ammoniacal liquid has been separated by filtration through cloth and by squeezing in a press, the solid residue is extracted with ten times its weight of 5 per cent. caustic soda solution, with which it is first macerated in the cold for ten to twelve hours, and then heated in a reflux apparatus on a water-bath for six hours. The mass is next filtered through cloth and the residue pressed and washed several times with water until the total volume of solution obtained is equal to that of the caustic soda solution used.

This brown liquid is evaporated to some extent on a water-bath and is then treated in the cold with an equal volume of 90 per cent. alcohol. The voluminous, flocculent precipitate of *gum* (*pentosans*), thus obtained is collected on cloth, washed and purified by repeatedly dissolving in dilute acid and reprecipitating with alcohol, this procedure being continued until the gum leaves a minimal ash on incineration.

To pass from the pentosans to the pentoses, the moist gum is hydrolysed (Conneler and Tollens, 1892 and 1903) by digestion for 12 hours with 25 parts of water and 2·5 parts of hydrochloric acid of sp. gr. 1·19, the mixture being finally heated on a water-bath until the furfural reaction (red coloration with aniline acetate paper) begins to make its appearance (about two hours). After filtration of the cold liquid and neutralisation with lead carbonate (testing with Congo-red paper), a few drops of barium hydroxide are added and the liquid filtered to remove precipitated lead chloride and barium carbonate. The solution is concentrated on a water-bath under reduced pressure, mixed with a little alcohol, filtered and concentrated to a syrup. This is taken up with methyl alcohol and the solution filtered to remove mineral and other impurities. The alcohol is then evaporated and the residue seeded with a few crystals of xylose or arabinose and left in a desiccator until the whole mass crystallises (this sometimes requires several weeks).

In order to separate the arabinose and xylose, which often occur together, Ruff and Ollendorff (1899) treat the mixed pentoses with eight times their weight of 75 per cent. alcohol and nearly their own weight of benzylphenylhydrazine dissolved in a little absolute alcohol. After several weeks' rest with frequent shaking, there separates *arabinose benzylphenylhydrazone*, which, in the pure state melts at 174° and, when treated with excess of formaldehyde, liberates the arabinose; the latter is soluble in water, whilst formaldehyde benzylphenylhydrazone remains undissolved.

The aqueous arabinose solution, after separation and concentration to a syrupy consistency, deposits *pure arabinose* in crystals The corresponding hydrazone of xylose is soluble in 75 per cent. alcohol, and yields xylose when decomposed with formaldehyde in the manner described above. The xylose can also be separated, according to Bertrand and Tollens (1900), by treating the mixture of pentoses with 2 parts of water, 1 part of cadmium carbonate, and 0·5 part of bromine. The mixture is heated for a short time on the water-bath, then left for twelve hours, evaporated, taken up with water, filtered, again evaporated, and mixed with alcohol; this procedure yields crystals of *cadmium bromoxylonate*, $C_5H_9O_6BrCd$. But before carrying out this separation, it is necessary to make sure that the mixture contains no galactose or glucose. These sugars can be detected by oxidising the mixture with nitric acid (sp. gr. 1·15) on the water-bath and evaporating the liquid to two-thirds of its volume. If the liquid remains turbid in the cold, the presence of *mucic acid*, derived from *galactose*, is indicated; and if, after neutralising with potassium carbonate, acidifying with acetic acid and concentrating, potassium hydrogen saccharate separates, the presence of *glucose*—which gives *saccharic acid* on oxidation—is demonstrated.

Arabinose and xylose are aldoses, $OH\cdot CH_2\cdot [CH(OH)]_3\cdot CHO$. By bromine water these two pentoses are oxidised with formation respectively of *arabonic* and *xylonic acids*, $OH\cdot CH_2\cdot [CH\cdot OH]_3\cdot CO_2H$, which are stereoisomeric; with more energetic oxidising agents, they give *trihydroxyglutaric acid.* On reduction they yield the corresponding alcohols, *arabitol* and *xylitol* (*see* p. 189), which are also stereoisomerides. By way of the corresponding cyanohydrins they can be converted into hexoses (*via* hexonic acids). All these reactions aid in establishing the constitution of these pentoses.

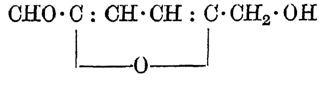
As they contain asymmetric carbon atoms, these sugars are optically active, and they exhibit the phenomenon of *muta-rotation;* thus, for freshly prepared solutions of xylose, the value of the specific rotation is $[\alpha]_D = 75°$ to $80°$, while five minutes after the sugar is dissolved it has the stable rotation $+ 19°$.

When pentoses are boiled with dilute sulphuric acid or with hydrochloric acid of sp. gr. 1·06 (12 per cent.), they yield *furfural*, $C_4H_3O\cdot CHO$ (aldehyde), which distils over and gives a characteristic and intense red coloration with aniline and hydrochloric acid, a phenylhydrazone with phenylhydrazine, and a slightly soluble condensation product with phloroglucinol.[1]

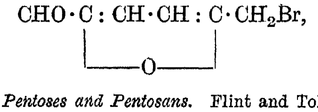
Treatment of any pentose or hexose with caustic soda in presence of air or other oxidising agent (*e.g.* HgO) yields no trace of saccharic acid, but gives formic acid and monobasic hydroxy-acids (*e.g.* glycollic, dl-glyceric, trihydroxybutyric, and various pentonic and hexonic acids); if air is excluded, aldotetroses, formaldehyde, a little 2 : 3-dienols, bioses, and glyceraldehyde are mainly formed.

Recent work has shown that the furfural obtained on distillation of vegetable substances with 12 per cent. hydrochloric acid is derived not merely from true pentosans, but also from oxycellulose, glycuronic acid, &c.; methylpentosans give methylfurfural. Hence Cross and Bevan suggest the name *furfuroids* for substances other than true pentosans which give furfural. On the other hand, it has been proposed by Tollens that the term *pentosan* be applied to the whole of the substances (furfuroids and true pentosans) which give furfural when distilled with 12 per cent. hydrochloric acid. *Hydroxymethylfurfural* (*see below*) does not distil in presence of acids but undergoes resinification, and hence escapes the Tollens method of estimating furfural.

Until comparatively recent times it was assumed that the pentosans were derived from the hexoses and polyhexoses, since it was known that 4-*hydroxymethylfurfuraldehyde*,



is obtained on heating levulose, d-mannose, d-glucose, d-galactose, chitose, &c., in a sealed tube with 0·3 per cent. of oxalic acid, while 4-*bromomethylfurfural*,



[1] *Quantitative Determination of Pentoses and Pentosans.* Flint and Tollens (1902) distil in a flask similar to that shown in Fig. 17 (p. 11), about 5 grms. of the substance with 100 c.c. of 12 per cent. hydrochloric acid, the heating being carried out in an oil-bath at 160°. Thirty c.c. of liquid are distilled over every twelve to fifteen minutes, in which time 30 c.c. of fresh acid are added by means of a tapped funnel, this procedure being continued as long as the distillate reddens a strip of filter-paper moistened with an acetic acid solution of aniline. To the distillate is added an excess (double the amount of furfural expected) of pure phloroglucinol dissolved in 12 per cent. hydrochloric acid. The volume of the liquid is made up to 400 c.c. with the same acid in a graduated flask, which is well shaken and left for 12 hours, at the end of which time the precipitate is collected on a tared filter, washed with 150 c.c. of water, dried for four hours in an oven and weighed. The weight of furfural is obtained by dividing this weight by a variable factor, which has the following values for different amounts (in grms.) of the phloroglucinol compound. 0·20 (1·820); 0·22 (1·839); 0·24 (1·856); 0·26 (1·871); 0·28 (1·884); 0·30 (1·895); 0·32 (1·904); 0·34 (1·911); 0·36 (1·916); 0·38 (1·919); 0·40 (1·920); 0·45 (1·927); 0·50 (1·930); 0·60 or more (1·931). The xylan is calculated by multiplying the quantity of furfural by 1·64, the araban, by 2·02, while for mixed pentosans, the factor 1·84 is employed.

Another method of procedure consists in precipitating the furfural with phenylhydrazine and estimating the nitrogen in the precipitate.

Jolles (1906), however, neutralises almost completely (to methyl orange) the distillate containing the furfuraldehyde, then adds 10 c.c. (more, if necessary) of a decinormal sodium bisulphite solution, and after two hours titrates the excess of bisulphite with a decinormal iodine solution (1 c.c. of which corresponds with 0·0075 grm. pentose).

is obtained by heating levulose (or filter-paper, cotton, cellulose, straw, starch, dextrose, lactose, glycogen, &c.) under pressure with chloroform saturated at 0° with hydrogen bromide. Further, when the oxime of levulose is heated with concentrated caustic potash solution, the nitrile is first formed and then hydrocyanic acid and d-arabinose :

$$OH \cdot CH_2 \cdot [CH \cdot OH]_4 \cdot CH : NOH \longrightarrow H_2O + OH \cdot CH_2 \cdot [CH \cdot OH]_4 \cdot CN$$
$$\longrightarrow HCN + OH \cdot CH_2 \cdot [CH \cdot OH]_3 \cdot CHO.$$

Oxidation of d-gluconic acid with peroxides also gives d-arabinose.

Ketohexoses in general, when heated with *dilute* acids (*e.g.* with 0·3 per cent. of oxalic acid under a pressure of 3 atmos.), are largely transformed into hydroxymethylfurfural, whilst the *aldohexoses* undergo this change only to a very slight extent ; if mineral acids are used, or oxalic acid in larger quantity, levulinic acid is obtained instead of hydroxymethylfurfural.

U. Nef's recent work (1910) tends to show that, in plants, pentosans cannot be derived from the hexoses, but that they are formed rather from either aldotetroses and formaldehyde or 2-carbon-atom sugars and glyceraldehyde. The *hexoses*, in their turn, would be formed, not from pentoses and formaldehyde, but rather from 2 mols. of glyceraldehyde or 3 mols. of a 2-carbon-atom sugar, or even from 1 mol. of a 2-carbon-atom sugar and 1 of an aldotetrose.

XYLOSE is readily obtained by boiling with dilute sulphuric acid plants containing it, especially jute, bran, straw, or, better still, apricot stones or maize husks. It bears also the name of *wood-sugar*, and is yielded by the decomposition of gluconic acid.

When pure, it crystallises and forms a phenylosazone melting at 160°.

d-**ARABINOSE** is lævo-rotatory, but is obtained from calcium d-gluconate and hydrogen peroxide and from d-glucose. In the pure state it forms prismatic crystals.

i-**ARABINOSE** is the optically inactive racemic isomeride, and is found in the urine of persons suffering from *pentosuria*.

l-**ARABINOSE** is obtained by boiling vegetable gum with dilute sulphuric acid. It is dextro-rotatory, but is designated a lævo-compound because it is related chemically to l-glucose. It forms sweet-tasting crystals melting at 160°, and its phenylosazone melts at 157°.

Two other pentoses are : **RIBOSE**, which, with nascent hydrogen, gives *adonitol* (a pentahydric alcohol, $OH \cdot CH_2 \cdot [CH \cdot OH]_3 \cdot CH_2 \cdot OH$, and the only *sugar-alcohol* yet discovered in plants, the leaves of which are able to transform it into starch ; the sap of *Adonis vernalis* contains as much as 4 per cent. of adonitol) ; and d-lyxose, which is obtained from galactonic acid and melts at 101°.

Higher homologues are the **Methylpentoses** : **FUCOSE**, contained in algæ ; **CHINOVOSE, ISORHAMNOSE,** and **RHAMNOSE** (or **Isodulcite**), $C_5H_9O_5 \cdot CH_3$, which is obtained by boiling quercetin and other glucosides with dilute sulphuric acid.

According to Rosenthaler (1909), **Methylpentose** in presence of pentoses can be recognised by heating the solution for a few minutes on a boiling water-bath with HCl of sp. gr. 1·19 and observing the yellow liquid thus obtained in the spectroscope : methylfurfural, from methylpentose (even as little as 0·0005 grm.) gives absorption bands between the blue and green. The reaction is still more sensitive if a little acetone is added before heating, the liquid then being coloured red (by the methylfurfural) and giving a sharp absorption band in the yellow (D line) ; pentoses do not give this reaction if the liquid is heated. Other sensitive reactions are obtained with phloroglucinol, orcinol, resorcinol, pyrogallol, aniline acetate, &c.

HEXOSES, $C_6H_{12}O_6$

These are of frequent natural occurrence and exist in various optically active stereoisomerides, since they contain four asymmetric carbon atoms, while they also form inactive racemic compounds. They are substances of sweet taste, and are extremely soluble in water, but in alcohol they dissolve but slightly and in ether not at all ; they crystallise with great difficulty and decompose when distilled. Their phenylhydrazones are soluble, and their phenylosazones insoluble in water. When boiled with hydrochloric acid they all give

(1) **Levulinic Acid** ($CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H$), the silver salt of which forms characteristic crystals, and (2) a brown amorphous mass of so-called *humic substances*. With methyl alcoholic ammonia, the hexoses form **Osamines** *e.g.* **Glucosamine**, $C_6H_{11}O_5 \cdot NH_2$.

They reduce Fehling's solution or ammoniacal silver solution in the hot, and with oxidising agents they yield hexonic acids and then lower acids down to oxalic.

With lime they form additive compounds decomposable by carbonic acid; with boiling milk of lime they turn brown and give **Hexosaccharine** (lactone of saccharic acid), $C_6H_{10}O_5$. By the combined action of concentrated sulphuric and nitric acids, they are converted into *pentanitrates*, while with alcohols and gaseous hydrogen chloride they form ethers (*glucosides*). The aldohexoses give the fuchsine-sulphurous acid reaction (*see* p. 206), which is, however, not shown by the ketohexoses. The mode of formation of the phenylosazones is described on p. 427.

With hydroxylamine they form oximes, *e.g.* *d*-**Glucosoxime**, which can be converted into the corresponding nitrile and then, by elimination of HCN, into the aldopentose (*d-arabinose*).

The hexoses are formed in various organisms and can also be obtained by hydrolysing polyhexoses with dilute acids or enzymes.

The optical activity of the hexoses indicated by the prefixes d-, l-, and i- indicates the sign of that of the substances with which they are connected genetically, but the fact that the actual direction of the rotation does not always correspond with this prefix is a source of some confusion. It must also be noted that the rotatory powers of the hexoses and pentoses are lowered when the sugars are dissolved in a centinormal alkali solution at 37°.

Synthetically the hexoses can be obtained from formaldehyde (*see* Note, p. 428), as well as from the hexahydric alcohols by gentle oxidation and from the hexonic acids by reduction. E. Fischer has synthesised d-glucose completely from glycerine, by way of (1) glyceraldehyde, (2) inactive fructose, which, with hydrogen, yields (3) inactive mannitol, oxidation of this giving (4) mannose and (5) racemic mannonic acid, the latter being resolved into its (6) active components by means of strychnine; d-mannonic acid, in presence of pyridine and water in the hot, produces (7) d-gluconic acid and this, on reduction, *d-glucose.*

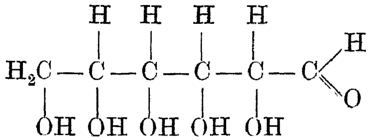
The relations between hexoses and pentoses were indicated in the last Note (*see* p. 429).

As was mentioned above, *fermentation* with yeast occurs only with d-glucose, d-fructose, d-galactose, d-mannose, and glycerose, no fermentation taking place with sorbose, the pentoses, l-glucose, l-fructose, l-mannose, or d-mannoheptose. So that only the stereoisomerides of a certain group are fermentable.

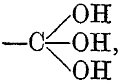
The *structures* of the hexoses are deduced partly from their general reactions and partly from the following facts:

The *chain* of six carbon atoms in the hexoses is *normal*, since reduction with hydrogen yields a hexahydric alcohol, which is further reduced by heating with hydriodic acid to normal sec. hexyl iodide, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CHI \cdot CH_3$; the constitution of the latter is shown by the fact that the corresponding secondary alcohol is oxidised to n-propylacetone, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH_3$, this, on oxidation, giving finally butyric and acetic acids of known constitution.

The hexoses contain five hydroxyl groups, as they yield pentacetyl-derivatives when boiled with acetic anhydride and sodium acetate or zinc chloride. Their constitutional formula hence cannot be other than:



since, if two hydroxyl groups were at any moment united with one carbon atom, a molecule of water would be eliminated immediately. Further, with hydrogen the hexoses form *hexitols,* which are not aldehydic but only alcoholic in character and do not give up H_2O under any conditions, so that two hydroxyl groups are not combined with one carbon atom. Neither can it be supposed that three hydroxyl groups are united with the terminal carbon, thus:



, because if this were so water would be readily separated and an acid formed, in which case the aqueous solution should conduct the electric current and have a dissociation constant much greater than that of acetic acid ; but this is not found to be the case.

Combination with bases does occur (with the hexabioses), but the compounds formed are additive compounds.

Since then there are a number of different hexoses, all showing the same general behaviour, they must have the same constitution, the differences being due to differences in the spatial structure.

Theoretically, 16 active stereoisomeric aldo-hexoses are possible, and 14 of them have been already prepared. The rotatory powers of the *phenylosazones* and *phenylhydrazones* may be of opposite signs to those of the corresponding hexoses.

d-**GLUCOSE** (**Grape Sugar, Dextrose, Starch Sugar**), $C_6H_{12}O_6$, is an aldose found in abundance in grapes and many other sweet fruits in company with d-fructose ; it also occurs in the urine of diabetic patients. It crystallises from water with $1H_2O$, which it loses at 120°, and from alcohol in the anhydrous form, melting at 146°. In aqueous solution it has the specific rotation + 53° at a temperature of 20°, but it exhibits muta-rotation, the rotatory power being about double the above value in freshly prepared solutions which have not been boiled. Owing to its rotatory power, glucose can be estimated polarimetrically (*see later*, Sugar).

When saccharose (a dextro-rotatory hexabiose) is heated with dilute acid, it is converted into a lævo-rotatory mixture of equal proportions of glucose (+) and fructose or levulose (−), which bears the name **Invert Sugar**, the change being known as *inversion*, since it is accompanied by alteration of the sign of the optical rotation.

On oxidation, d-glucose gives *d*-**Gluconic Acid**, $OH \cdot CH_2 \cdot [CH \cdot OH]_4 \cdot COOH$, and then the dibasic **Saccharic Acid**, $CO_2H \cdot [CH \cdot OH]_4 \cdot CO_2H$, which, like tartaric acid, gives a slightly soluble acid potassium salt ; the latter serves to characterise d-glucose, it being sufficient to oxidise with nitric acid and then precipitate the saccharic acid with saturated potassum acetate solution. When reduced, d-glucose yields *d-sorbitol* (hexahydric alcohol).

The sugar forms a phenylosazone, melting at 204° to 205°, and two phenylhydrazones, melting respectively at 115° and 144°.

When heated above 140°, glucose is converted into *caramel.*

In dilute solution it reduces Fehling's solution in the hot, and on this reaction is based the estimation of glucose.[1]

[1] **Estimation of Glucose.** In the chemical way the estimation is effected by means of Fehling's solution by the method described later in the section on Saccharose, about 10 grms. of solid glucose or 15 to 20 grms. of the syrupy product being dissolved in water, made up to 100 c.c. in a graduated flask and filtered through a dry, covered filter. Polarimetric estimation is not usually applicable owing to the presence of dextrin, sometimes to the extent of 40 per cent., this increasing the rotation. The *dextrin* is determined by dissolving 5 grms. of the glucose in 400 c.c. of water, adding 40 c.c. of HCl of sp. gr. 1·125, heating for two hours on a boiling water-bath, cooling, neutralising exactly with NaOH and making up to 500 c.c. The total dextrose (including that formed by hydrolysis of the dextrin) in this solution is now determined by means of Fehling's solution. The difference between the amounts of glucose found before and after the action of acid, multiplied by 0 9, gives

Barfoed has proposed the following reaction for detecting the presence of minimal quantities of *glucose* (0·2 mgrm.) mixed with lactose, maltose, dextrin, and saccharose: to 5 c.c. of Barfoed's reagent (an acetic acid solution of normal cupric acetate) in a test-tube is added the dilute aqueous sugar solution (about 1 per cent.), the mixture being heated on a boiling water-bath for 3½ minutes, allowed to cool for 10 minutes, and filtered. If the filter retains red cuprous oxide, the presence of dextrose is demonstrated.

MANUFACTURE OF GLUCOSE. One hundred kilos of starch are mixed with 500 litres of water containing 5 kilos of concentrated sulphuric acid, and the mass heated to 40° to 50° and then introduced into a suitable autoclave or converter (conical or cylindrical, capable of withstanding 6 atmos.), coated internally with lead and externally with insulating material. A current of steam is then passed in and the temperature raised to 160°. By allowing the steam to escape after this temperature has been reached, the empyreumatic oils (which are of disagreeable odour) are carried away; the steam is condensed in cooled coils (the heat being used to heat water). The temperature of the mass is then maintained at 80° until a test portion gives no blue colour with iodine and no precipitate with lead acetate (or potassium silicate), these being indications of the saccharification of the dextrin and gummy matters; a further sign of this is the non-formation of a precipitate with alcohol. The duration of the heating is 3 to 4 hours.

The mass is then decanted into the neutralisation vats, which are furnished with stirrers, and finely divided calcium carbonate, suspended in a large quantity of water, gradually added in order to neutralise and precipitate the sulphuric acid. After thorough mixing of the mass, it is allowed to settle and the liquid then decanted into another vessel, where the calcium sulphate remaining in solution is precipitated by the addition of a little ammonium oxalate.

The liquid is next filter-pressed, evaporated in a vacuum to 28° to 30° Bé., decolorised in the hot by means of dry blood mixed with powdered wood charcoal or by passing through vertical filters filled with the charcoal similar to those used in sugar refineries. It is then concentrated in a vacuum (*see* Sugar Industry) either to 41° to 42° Bé., to give solid compact glucose separating in the cooling vats (fitted with stirrers), or to about 65° Bé., when ready formed crystals of glucose are added. The temperature is lowered to 18° to 20°, and after 3 or 4 days the separated crystals centrifuged and so freed from the syrupy portion, which retains the dissolved dextrin and other impurities. To obtain *granulated glucose* the solution is concentrated only to 30° to 32° Bé.; after 8 to 10 days in the cold, a granular *hydrated glucose* separates.

When a very dense liquid glucose (so dense that its specific gravity cannot be determined with the ordinary hydrometers) is required, a little dextrin is left in the sugar so as to prevent crystallisation.

The theoretical yield of pure glucose from 100 kilos of dry starch is 110 kilos.

In some factories the starch is saccharified with a little nitric acid, which gives a less highly coloured syrup and is more rapid in its action. The nitric acid is then eliminated by means of sulphurous acid, which is oxidised at the expense of the nitric acid to sulphuric acid, this being readily precipitable with lime.

The advantages of transforming starch into glucose by means of hydrofluoric acid consist in a rapid and complete hydrolysis, ready separation of the whole of the acid as barium fluoride, and the production of a glucose with a pure flavour.

In 1901 Calmette found that, after heating crushed cereals with double the amount of

the quantity of dextrin. The acidity should not exceed 2 c.c. of normal caustic soda per 100 grms of syrup. The proportion of *ash* varies from 0·2 to 0·7 per cent.

Solid commercial glucose contains 65 to 75 per cent. of glucose and the liquid 35 to 45 per cent. In pure solution, glucose can be estimated by means of the specific gravity:

Density at 17·5°	Degrees Bé.	Per cent. of pure glucose	Density at 17·5°	Degrees Bé.	Per cent. of pure glucose
1·0192	2·7	5	1·1310	16·4	35
1·0381	5·3	10	1·1494	18·8	40
1·0571	7·5	15	1·1680	20·6	45
1·0761	10·1	20	1·1863	22·7	50
1·0946	12·4	25	1·2040	24·4	55
1·1130	14·6	30	1·2218	26·1	60

1 per cent. hydrochloric acid for 1 hour at 100°, 1 hour at 110°, and a third hour at 120°, and then cooling, the mass may be converted completely into glucose by the action of *Mucedinæ*.

USES. Large quantities of glucose are consumed for making sweet syrups, *caramel*,[1] fermented liquors, sweets and wine, preserving fruit, adulterating honey, dressing textiles, &c.

In 1909–1910 Italy possessed 15 glucose factories, producing 676 quintals of the solid and 65,000 of the liquid sugar ; the total revenue from the tax of manufacture amounted to £51,000, solid glucose paying 32*s*. and the liquid 16*s*. per quintal. The Customs duty is 40*s*. for liquid and 64*s*. for solid glucose per quintal. Importation is very small in amount and the exports only 300 quintals of liquid glucose. In the United States, where glucose is made from maize, the amount produced reached 800,000 quintals in 1907.

In France the 16 factories working in 1908 to 1909 produced 200,000 quintals of glucose, about 48,000 being used in breweries while 72,000 were exported.

England imported 46,500 tons (£462,940) of glucose in 1909 and 62,500 tons (£595,808) in 1910. The United States exported 90,000 tons, valued at £1,196,200, in 1911.

The output in Germany, with about 26 factories, was as follows (quintals) :

	Solid Glucose		*Glucose Syrup*		*Caramel*
	Produced	Exported	Produced	Exported	Produced
1897–1898	72,000	—	348,000	—	—
1901–1902	99,400	28,874	492,700	76,800	48,000
1902–1903	96,170	12,026	545,300	30,620	—
1903–1904	75,050	6,113	469,461	13,060	35,630
1904–1905	53,000	2,890	324,340	10,432	34,690
1905–1906	91,900	—	582,750	—	43,000
1906–1907	88,300	—	477,506	—	44,244
1907–1908	81,836	—	466,340	—	48,461
1908–1909	87,623	—	506,600	—	44,180

The diminished production in 1904–1905 was due to a poor potato crop and an over-production of beet-sugar, the less amount exported being caused partly by enhanced prices and partly by increased production in other countries.

Glucose syrup with a specific gravity of 42° Bé. is sold in Italy at 48*s*. to 52*s*. per quintal, whilst in Germany, where there is no manufacturing tax, it costs about 28*s*. ; the crystalline sugar costs rather more.

d-FRUCTOSE (Levulose, Fruit-Sugar) occurs abundantly, together with glucose, in sweet fruits, and is also found in large quantities in *honey* (which contains natural invert sugar). The hydrolysis of *inulin* (a polyhexose found in dahlia tubers) yields d-fructose alone. The sugar is *lævo-rotatory* and fermentable. It has the constitution of a *ketose*, $OH\cdot CH_2\cdot[CH\cdot OH]_3\cdot CO\cdot CH_2\cdot OH$, hydrolysis of its cyanohydrin giving the heptonic acid,

$$OH\cdot CH_2\cdot[CH\cdot OH]_3\cdot \underset{\displaystyle COOH}{\underset{|}{C}}(OH)\cdot CH_2\cdot OH.$$

The *phenylosazone* of d-fructose is identical with that of d-glucose.

Methylphenylhydrazine forms osazones only with ketoses and not with aldoses, with which, however, it forms colourless hydrazones, these being usually soluble and hence readily separable from the slightly soluble, intensely yellow osazones (*see* pp. 333 and 427).

[1] Caramel (or *sugar colouring*) is prepared by fusing and heating glucose or saccharose at a temperature of 160° to 200° (not beyond this) in an iron vessel fitted with a stirrer. To glucose 1 to 3 per cent. of soda is also added to accelerate the operation and to neutralise the acid formed (saccharose also yields acid, being first partly inverted by the heating), and after the change is complete, 50 per cent. of hot water is added and the mass well mixed and filtered through charcoal. A brown, syrupy mass is thus obtained which is soluble in water or alcohol, giving a brown or yellow solution according to the dilution.

That obtained from saccharose, which does not contain dextrin and dissolves completely in 80 per cent. alcohol, is used for colouring spirits, whilst that from glucose, which contains dextrin and is entirely soluble in 75 per cent. alcohol, is used to darken beer and vinegar. The presence of more than 5 per cent. of ash indicates that a caramel has been prepared from molasses ; good qualities contain only 1 per cent. of ash.

In Germany caramel is exempt from taxation and costs about 32*s*. per quintal (for the production, *see* above).

When phenylosazones are heated gently with hydrochloric acid, they lose 2 mols. of phenylhydrazine with formation of *osones* which contain two carbonyl groups. Thus phenylglucosazone yields **Glucosone, $OH \cdot CH_2 \cdot [CH \cdot OH]_3 \cdot CO \cdot CHO$,** and this when treated with nascent hydrogen (from zinc and acetic acid) takes up 2H at the terminal carbon atom, fructose being thus obtained from glucose. On the other hand, reduction of a ketose gives the corresponding hexahydric alcohol, which, on oxidation, yields the monobasic hexonic acid; the latter loses water, giving rise to the lactone, and this gives the aldose on reduction. d-Fructose is lævo-rotatory; $[\alpha]_D = -92^\circ$ at a temperature of 20°.

This sugar has been suggested for the use of diabetic and tuberculous patients and as a substitute for cane-sugar, since it is sweeter, and in syrups and honey it hinders the crystallisation of the other sugars.

In view of these uses, attempts have been made to prepare fructose industrially. Honig in 1895 and Steiner in 1908 proposed its extraction from endive roots and dahlia tubers (these contain from 8 per cent. to 17 per cent. of *inulin*). The crushed tubers are treated in the hot (below 65°) with a little milk of lime and with steam, and are then pressed. The juice, after defecation with clay, is allowed to crystallise in a rotating cooler, the mass of inulin crystals being centrifuged, redissolved in hot water, and converted into fructose by means of dilute acid (*see* Glucose); the fructose solution is concentrated in a vacuum. Steiner calculates that the sugar can be made by this process at a cost of 1*s.* per kilo.

A *characteristic reaction* for the detection of fructose in presence of other reducing sugars is obtained with the following solution: to a solution of 12 grms. of glycocoll in hot water are slowly added 6 grms. of pure cupric hydrate, the liquid being heated on a water-bath for about 15 minutes until complete solution takes place and then cooled to 60°; after 50 grms. of potassium carbonate have been added, the volume is made up to 1 litre and the whole filtered. This reagent is reduced in the *cold* only by levulose (1 to 5 per cent. solution), the time required varying from 4 to 9 hours; other sugars, including the pentoses, reduce it only at temperatures above 40°.

d-**MANNOSE, $C_6H_{12}O_6$,** is an aldose stereoisomeric with glucose, and is fermentable; it is obtained from mannitol, the corresponding alcohol, by oxidation. It melts at 195° to 200°, and differs from other monoses in forming a phenylhydrazone only slightly soluble in water. With oxidising agents it forms first monobasic *d-mannonic* acid and then dibasic *d-mannosaccharic* acid, $COOH \cdot [CH \cdot OH]_4 \cdot COOH$.

A general method for converting one hexose into a stereoisomeric one, *e.g.* d-mannose into d-glucose, is as follows: the d-mannose is oxidised to d-mannonic acid and the latter dissolved in quinoline and the solution boiled; in this way the acid undergoes partial transformation into the stereoisomeric d-gluconic acid, reduction of the lactone of which yields d-glucose. The reverse change of d-gluconic into d-mannonic acid is also produced to some extent by boiling with quinoline, so that d-glucose can be converted into d-mannose. These sugars (and acids) differ only in the space arrangement of the groups united with the asymmetric carbon atom in the α-position, $OH \cdot CH_2 \cdot [CH \cdot OH]_3 \cdot \underset{\alpha}{C}H(OH) \cdot CHO$, since the phenylosazone of d-mannose is identical with that of d-glucose,

$$\begin{array}{l} OH \cdot CH_2 \cdot [CH \cdot OH]_3 \cdot C \cdot C{:}N \cdot NHC_6H_5. \\ \qquad\qquad\qquad\qquad\quad \| \\ \qquad\qquad\qquad\qquad\quad N \cdot NHC_6H_5 \end{array}$$

It is this α-carbon atom, adjacent to the aldehyde group, which is influenced when a hexonic acid is boiled with quinoline or pyridine.

When glucose, fructose, or mannose is treated with a very dilute alkali solution, a mixture of all three sugars results. The fructose seems to be an intermediate product, since the dextro-rotation of mannose gradually changes to a lævo-rotation, owing to formation of fructose, the amount of the lævo-rotation subsequently diminishing as the fructose becomes converted into glucose.

l-**MANNOSE** and *l*-**GLUCOSE, $C_6H_{12}O_6$ (Aldoses),** are obtained together from l-arabinose by the cyanohydrin synthesis and reduction of the lactones of the resulting acids. Application of this synthesis to an aldehyde yields, in general, two optically active stereoisomerides, since a new asymmetric carbon atom is created and the chances of formation of the two isomerides are equal. But the final mixture will be inactive only when the initial molecule is inactive, while, when this is optically active (as with arabinose), the mixture will be active, as the components will not have equal and opposite activities;

one of these will have a rotation greater than that of the original molecule by a certain amount and the other a rotation less by the same amount.

d-**GALACTOSE**, $C_6H_{12}O_6$ (Aldose), is obtained by oxidising dulcitol, $C_6H_8(OH)_6$, or by hydrolysing milk-sugar, in which case it is formed together with glucose. It melts at 168°, is fermentable, and exhibits muta-rotation. It is an aldose, giving on oxidation first monobasic *d-galactonic acid* and then dibasic *mucic acid*, $COOH \cdot [CH \cdot OH]_4 \cdot COOH$, which is inactive.

HEPTOSES, OCTOSES, and **NONOSES** have not been found in nature, but are prepared synthetically from mannose by means of the cyanohydrin synthesis.

GLUCOSIDES

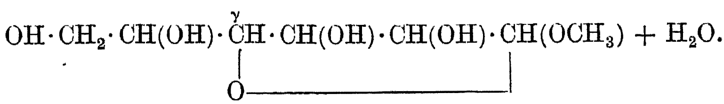
These are of frequent occurrence in the vegetable kingdom and, when heated with acid or alkali or subjected to the action of certain enzymes, decompose into a glucose and an alcohol (or phenol, aldehyde, or nitrogen compound); they are hence ethereal derivatives of the monoses (*e.g.* **Amygdalin, Salicin, Populin, Coniferin,** &c.).

Artificial glucosides have been prepared by E. Fischer by the interaction of an alcohol and a monose in presence of hydrochloric acid (which withdraws water). The glucosides are analogous in structure to the *acetals*

$$R \cdot C \begin{matrix} \diagup H \\ \diagdown O \end{matrix} + 2CH_3 \cdot OH = H_2O + R \cdot C \begin{matrix} \diagup H \\ -OCH_3 \\ \diagdown OCH_3 \end{matrix} \text{ (acetal)},$$

but only 1 molecule of alcohol takes part in the reaction:

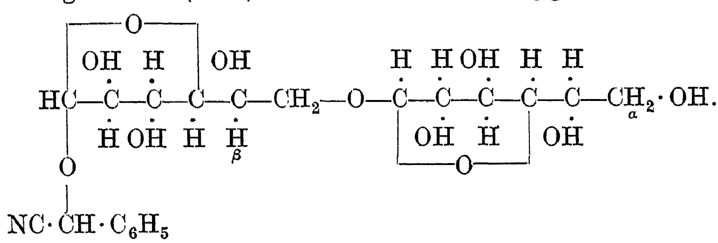
$$OH \cdot CH_2 \cdot CH(OH) \cdot \underset{\gamma}{C}H(OH) \cdot \underset{\beta}{C}H(OH) \cdot \underset{\alpha}{C}H(OH) \cdot CHO + CH_3 \cdot OH =$$



Glucoside

The glucosides are readily resolved into their components, so that union of these directly through carbon atoms is excluded. The combination with the oxygen of the hydroxyl in the γ-position is deduced from analogous reactions, such as formation of lactones. The constitution of bioses is explained similarly (*see later*).

According to Auld (1908) the constitution of **Amygdalin** is as follows:



Ciamician and Ravenna (1908) showed that, when glucosides are introduced into plants (maize and beans), they are absorbed and transformed without producing any effect, whilst the decomposition products of the glucosides (benzaldehyde, salicylic alcohol, hydroquinone, &c.) act as poisons. Hence the formation of glucosides in plants seems to have the effect of paralysing the poisonous action of certain substances. The same authors (1909) found that, when maize is made to absorb *saligenin*, this is partly transformed into its glucoside, *salicin*; in a similar manner they obtained *benzylglucoside* (1911).

B. HEXABIOSES

Almost all of the bioses at present known decompose into hexoses (either two different monoses or 2 mols. of one and the same monose). No biose gives a hexose and a pentose.

This decomposition of bioses, which is known as *hydrolysis*,

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6,$$

can be effected by boiling with dilute acid or by the action of enzymes ; and since it takes place with great readiness, it is assumed that the constituent monoses of the bioses are united, not between carbon atoms, but more probably between oxygen atoms. It would appear, however, that the hydrolysis is not a unimolecular reaction (*see* vol. i, p. 66).

Synthetic bioses are obtained by treating, for instance, a hexose with acetyl chloride, the resulting *acetochlorhexose*, in presence of sodium alkoxide and a hexose, giving the acetyl derivative of a biose ; elimination of the acetyl group by means of soda then yields the biose itself.

Bioses may also be obtained by the action of certain enzymes on monoses ; thus, with *maltase*, glucose gives *isomaltose* (not, as was formerly thought, maltose ; *see* p. 113). The *lactase* of kephir acts on a mixture of glucose and galactose, giving *isolactose :* with glucose alone it yields a different biose. Glucose and galactose may also be condensed by the action of *emulsin* (*see* p. 113).

Of the hexabioses, maltose, lactose, and saccharose will be considered (for *melibiose, see later, under* Raffinose).

MALTOSE forms crystals of the formula $C_{12}H_{22}O_{11} + H_2O$ and is strongly dextrorotatory. As was seen in considering the manufacture of alcohol and of beer, it is prepared industrially from starch by the action of diastase (*see* pp. 111, 112).

Hydrolysis of maltose by dilute acid yields only d-glucose. It gives reactions similar to those of the monoses. Thus, it reduces Fehling's solution, and with phenylhydrazine forms phenylmaltosazone, $C_{24}H_{32}O_9N_4$. On oxidation it yields monobasic **Maltobionic Acid,** $C_{12}H_{22}O_{12}$, which gives *d*-**Gluconic Acid,** $OH \cdot CH_2 \cdot [CH \cdot OH]_4 \cdot COOH$, on hydrolysis. Hence maltose contains only one carbonyl group and not the two corresponding with the 2 constituent glucose molecules, the phenylosazone being formed with 2, and not 4, mols. of phenylhydrazine, while oxidation of the sugar yields a monobasic and not a dibasic acid. Hence the 2 mols. of glucose in the maltose molecule are joined in such a way that only one carbonyl group remains free to exert its characteristic reactions, the other serving to link up the 2 glucose molecules. It is usual to include between brackets the monose residue which has no free carbonyl owing to the oxygen atom of this group being joined to the other monose residue, and to place outside the brackets those monose residues which retain free carbonyl. Maltose would then be represented by the formula $\underset{\text{d-glucose}}{(C_6H_{11}O_5 \cdot O)}\ \underset{\text{d-glucose}}{C_6H_{11}O_5}$. Maltose is not fermentable directly, the maltase of yeast first converting it into fermentable glucose (*see* p. 112).

Isomaltose is not fermentable.

LACTOSE (or **Milk-Sugar**), $C_{12}H_{22}O_{11} + H_2O$, is contained in milk (up to 5 per cent.) and is less sweet than cane-sugar. Its reactions are similar to those of the monoses (reduces Fehling's solution, &c.), and it yields d-glucose and d-galactose on hydrolysis. It does not ferment with beer-yeast, which contains no enzyme capable of hydrolysing it. The glucose residue has its carbonyl free, whilst the carbonyl of the galactose takes part in the union of the 2 monos emolecules, so that it will be represented thus : $\underset{\text{d-galactose}}{(C_6H_{11}O_5 \cdot O)}\ \underset{\text{d-glucose}}{C_6H_{11}O_5}$.

In fact, oxidation of lactose by means of bromine water results in the formation of monobasic *lactobionic acid,* which, on hydrolysis, gives d-galactose and d-gluconic acid.

Industrial Preparation. Unless a dairy has an average production of at least 60 to 80 hectols. of whey per day, it is not expedient to extract the milk-sugar. The preparation is now carried out as follows : The whey is treated immediately after the first coagulation of

the cheese.[1] The concentration is carried out in single or double-effect vacuum pans, similar to those used in sugar factories. Whey is passed continuously into the concentrator until the liquid attains a density of 30° Bé. in the hot (about 60 per cent. of the sugar). It is then collected in iron vessels holding about 700 litres, in which it is cooled by water circulating through a surrounding jacket. In the course of 24 hours, during which the mass is well stirred three or four times, the temperature is lowered to 20°. A pasty mass of fine crystals then separates, with an oily layer at its surface.

The crystals are separated by diluting the mass with a little cold water ($\frac{1}{5}$) and centrifuging, the crystals being retained in the drum of the centrifuge by means of a cloth. When a sufficient quantity of crystals has been thus collected in the basket of the centrifuge, the mass is washed with a gentle spray of cold water, the crude, slightly yellow sugar thus obtained representing 3·6 to 4·3 per cent. of the whey taken.

This *crude milk-sugar* contains 88 per cent. of sugar and 12 per cent. of water and various impurities (proteins, &c.). The liquid from the centrifuge still contains about 30 per cent. of the total sugar (not crystallised but forming a syrup). This liquid, which usually has a *density* of about 15° Bé., is heated to boiling by direct steam in a vessel with a flat, perforated false bottom, the albumin being thus coagulated. After half an hour's rest, the albumin collects as a compact layer at the surface, the liquid being then drawn off from below so as to leave the cake of albumin on the false bottom ; this is removed, pressed in bags, and given to pigs or mixed with white flour to make bread. The albumin-free liquid is concentrated in vacuum pans to 35° Bé. (measured in the hot) and allowed to cool for several days, with occasional stirring, in iron vessels. This procedure yields a dark pasty mass of the crystalline sugar, which is collected by diluting with a large quantity of *cold* water and centrifuging as before ; this sugar amounts to 0·3 to 0 7 per cent. of the original quantity of whey.

The *mean* yield of crude milk-sugar is 4·3 per cent. of the whey (the maximum of 4·8 per cent. being obtained in winter and the minimum of 3·9 per cent. in summer).

The liquid from the second crystallisation and centrifugation is not treated further, unless by osmosis ; it is preferably utilised as cattle-food, as it is rich in potassium salts, nitrogen, and phosphoric acid.

The crude sugar is either dried and placed on the market or subjected to a refining process. If left in heaps, it deteriorates to some extent.

The *refining* is carried out as follows: The sugar is dissolved, in an open boiler with a double bottom (heated by indirect-fire heat), in water at 50°, the liquid being well stirred so as to obtain a solution of 13° to 15° Bé. (24 to 27 per cent. of sugar). A little bone-black and about 0·2 per cent. (on the weight of sugar) of acetic acid are then added, and the heating continued until the boiling-point is approached, when magnesium sulphate (about 0·2 per cent.) is added and the liquid subsequently kept boiling for a few minutes. The mass suddenly froths very considerably (if necessary, the steam-cock is closed ; the boiler should not be too full initially) and the temperature rises to 105°. The charcoal decolorises the liquid and absorbs unpleasant flavouring substances, while the albumin is coagulated in large flocculent masses (by the acetic acid) and the phosphoric acid is precipitated by the magnesium. The hot liquid is filter-pressed, and the solid residue, after being washed with water and treated with a suitable amount of sulphuric acid, constitutes an excellent nitrogenous superphosphate. The clear liquid from the filter-press is concentrated as usual *in vacuo* to 35° Bé. in the hot (65 per cent. of sugar), the formation of froth being prevented. It is then crystallised, and when the maximum quantity of crystals has separated, these are separated by centrifuging, giving *first product*. After subsequent concentrations of the mother-liquor, *second* and *third* products are obtained. These three products together amount to about 3 to 3·5 per cent. of the original quantity of whey ; they may be kept separate or mixed and then recrystallised.

To obtain the sugar in the very white powdery form in which it is now sold, the refined product (first, second, or third) is dissolved in hot water to give a solution of 15° Bé., which is boiled and, after a little aluminium sulphate (0·1 per cent.) has been added, filter-pressed, the clear watery filtrate being concentrated to 32° Bé. It is then crystallised in copper vessels, centrifuged, and dried in revolving inclined drums round which hot water passes.

It is dry when it no longer adheres on compressing between the hands. The *cold* sugar

[1] Dairies not producing sufficient whey simply purify it by boiling with acid whey to coagulate the albumin and filtering. It is then despatched to works which treat it further.

is ground and sieved to an impalpable powder. The average yield over the whole year is 2·5 kilos of the powdered sugar per 100 litres of whey. This powder should be left in open vessels for some days, as, if packed immediately, it develops an unpleasant smell (which, however, it loses if spread out in the air).

To obtain the sugar in masses of aggregated crystals, solutions of the gravity 21° to 24° Bé. are crystallised in wooden vessels containing numbers of small wooden rods; the crystallisation sometimes occupies as much as a fortnight, and a liquid of 13° Bé. remains which can be concentrated anew.

The *albumin* separated when whey is boiled contains, after pressing, about 60 per cent. of water and 40 per cent. of dry matter composed of 17 per cent. of protein substances, 11 per cent. of milk-sugar, 2·3 per cent. of fat, 5 per cent. of ash (one-half of which is insoluble in water), and 1·7 per cent. of lactic acid.

The final mother-liquor, or *lactose molasses,* is brownish black, and contains about 73 per cent. of water, 6 per cent. of ash (two-thirds soluble in water), 0·10 per cent. of fat, 0·6 per cent. of nitrogen, 1·5 per cent. of acid (calculated as lactic acid), and 22·5 per cent. of substances which reduce Fehling's solution (calculated as milk-sugar).

The milk-sugar industry has undergone considerable development in Italy during recent years, the exports increasing from 446 quintals (£1516) in 1903 to 3087 quintals (£11,113) in 1905, and then falling to 137 quintals in 1910.

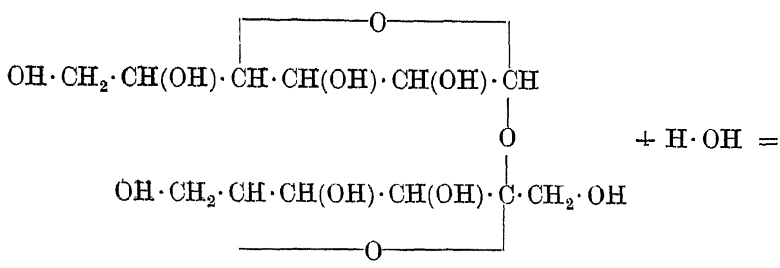
In 1905 Germany imported 2800 quintals (£13,300) and exported 5485 quintals (£28,800), while in 1909 the imports were only 135 and the exports 1650 quintals.

The price varies from 68*s*. to 96*s*. per quintal.

Tests for Milk-Sugar. Adulteration with mineral substances is recognised by the ash exceeding 1 per cent. in amount. When dextrin is present, this does not dissolve in alcohol, while the presence of glucose or saccharose (even as little as 2 per cent.) is indicated by evolution of carbon dioxide from a 10 per cent. solution of the sugar mixed with a little fresh beer-yeast and kept at 20° to 30° for 2 days; the invertase present in the yeast inverts the saccharose, which then ferments, but it does not break down the lactose, which consequently does not ferment. It is also found that when the *Bulgarian ferment* (*Bacterium bulgaricum*) acts on a mixture of saccharose and lactose, the latter alone is destroyed.

SACCHAROSE (Sucrose, Cane-sugar), $C_{12}H_{22}O_{11}$

Saccharose may be regarded chemically as the condensation product of two hexamonoses, glucose and fructose, which are generated by hydrolysis with dilute acid. The characteristic reactions of the monoses are lacking in saccharose, which does not reduce Fehling's solution, form osazones, or turn brown when treated with caustic soda solutions. It must therefore be assumed that the saccharose molecule contains no free carbonyl group (aldehydic or ketonic), the two such groups in the two monoses being annulled in the condensation. This is seen clearly from the following equation, in which a constitutional formula with the lactonic groupings so common to these substances (*see* p. 428) is attributed to saccharose:



Saccharose

$$OH \cdot CH_2 \cdot [CH \cdot OH]_4 \cdot C\Big\langle{}^{O}_{H} + OH \cdot CH_2 \cdot [CH \cdot OH]_3 \cdot CO \cdot CH_2\ OH.$$

Glucose Fructose

The rational formula (*see* Maltose) of saccharose will hence be :

$$(C_6H_{11}O_6 \cdot O \cdot C_6H_{11}O_5).$$

Saccharose and the bioses generally are not changed by the direct action of alcoholic ferments or of the majority of enzymes, so that they cannot be converted immediately into alcohol and carbon dioxide, as is the case with the hexoses. In order that alcoholic fermentation of cane-sugar may take place, it is necessary that the sugar should be first inverted by the *invertase*—almost always present in yeasts—into fermentable glucose and fructose. Hence, yeasts which contain no invertase cannot ferment saccharose. *Saccharomyces octosporus*, for instance, leaves this sugar unchanged, although it ferments maltose, owing to the presence of *maltase*, which hydrolyses the maltose to glucose.

It has already been mentioned that saccharose is readily hydrolysed by heating with a minimal quantity of a dilute mineral acid, and that this hydrolysis is known as *inversion* (*see* p. 433) because the dextro-rotatory saccharose ($[\alpha]_D = +66 \cdot 5°$) is changed into a lævo-rotatory mixture of equal proportions of glucose and fructose (*invert sugar*). The *velocity of inversion*, s, is proportional to the amount of cane-sugar present in the solution at any moment, and is hence expressed by $s = k\ (p - x)$, where p is the quantity of the original sugar and x that which has already undergone inversion. The *inversion constant*, k, varies with the nature of the acid employed and is proportional to the degree of electrolytic dissociation of the acid, the rate of inversion increasing with the number of free hydrogen ions. It is, indeed, possible to determine the *ionic concentration* of an acid solution by means of the velocity of inversion, or the amount of reducing sugar formed in unit time, in a saccharose solution of definite concentration. In the cold, sulphurous and carbonic acids have scarcely any inverting power.

Saccharose melts at 160° and, on solidification, forms an opaque, amorphous, glassy mass, which then crystallises in inclined monoclinic or rhombic prisms with blunted angles ; at a higher temperature it caramelises to a brown mass with evolution of gas (*see* p. 435). It has the sp. gr. 1·5813.

One part of water dissolves 2·5 parts of saccharose at 0° and 4·5 parts at 100°. It is almost insoluble in absolute alcohol or ether, but dissolves slightly in methyl alcohol. It readily forms supersaturated aqueous solutions, which then rapidly deposit anhydrous crystals ; this phenomenon is utilised in its industrial preparation.

Cane-sugar forms compounds (*sucrates*) with inorganic bases ; thus, with lime it forms (1) **Monocalcium Sucrate**, $C_{12}H_{22}O_{11}$, CaO, $2H_2O$, soluble in water, (2) **Dicalcium Sucrate**, $C_{12}H_{22}O_{11}$, $2CaO$, also moderately soluble in water, and, on heating a solution of either of these compounds, (3) **Tricalcium Sucrate**, $C_{12}H_{22}O_{11}$, $3CaO$, $3H_2O$, insoluble in water.

The manufacture of cane-sugar is described later.

A sensitive reaction for the detection of small quantities of sugar is indicated on p. 447.

Pozzi-Escot (1909) has devised a still more sensitive reaction for the sugars : into a test-tube are introduced 2 c.c. of the aqueous solution, 1 c.c. of 5 per cent. ammonium molybdate solution and, after mixing, 10 to 12 c.c. of concentrated sulphuric acid, which is poured carefully down the side of the tube. The formation of a blue ring within 20 minutes indicates the presence of more than 0·0005 per cent. of sugar ; and if the blue ring appears within 30 minutes when the upper part of the liquid is heated to boiling, the solution contains at least 0·00002 per cent. of sugar.

C. TRIOSES

RAFFINOSE, $C_{18}H_{32}O_{16} + 5H_2O$, forms pointed crystals and has a very high rotatory power ($[\alpha]_D^{20} = +104 \cdot 5°$), and since also saccharose containing raffinose exhibits pointed crystals and an increased rotation, raffinose is known in Germany as *Spitzenzucker* or *Pluszucker*. It is a hexatriose, and when hydrolysed takes up $2H_2O$, giving equal proportions of d-glucose, d-fructose, and d-galactose. By restricting the hydrolysis, most suitably by effecting it with enzymes, an intermediate stage may be realised, consisting of d-fructose and *melibiose* (isomeric with lactose), which is subsequently resolved into d-glucose and d-galactose. Raffinose is found together with cane-sugar in the sugar-beet, its amount varying with the season. In the manufacture of saccharose, it accumulates in the molasses and often occurs abundantly in the sugar extracted from beet-molasses by the strontia process ; in the final syrup from this treatment it occurs sometimes to the extent of 20 per cent. Raffinose does not give the reactions of the monoses (reduction of Fehling's solution, &c.), and hence contains no carbonyl group, its rational formula being

$$\underset{\text{Galactose}}{(C_6H_{11}O_5 \cdot O)} \cdot (\underset{\text{Glucose}}{C_6H_{10}O_4} \cdot O \cdot \underset{\text{Fructose}}{C_6H_{11}O_5}).$$

Melibiose, which, like lactose, exhibits the reactions of the monoses and contains a carbonyl group, is represented thus: $\underset{\text{Galactose}}{(C_6H_{11}O_5 \cdot O)} \cdot \underset{\text{Glucose}}{C_6H_{11}O_5}$. So that raffinose usually decomposes first at the point where a carbonyl group occurs (between glucose and fructose) ; otherwise it would yield a biose without a free carbonyl group. Recently, indeed, Neuberg (1907) has shown that the action of emulsin on raffinose gives galactose and cane-sugar (which does not give the monose reactions), this decomposition thus occurring at the opposite end of the molecule. This observation supports Herzfeld's hypothesis that in the beet raffinose is formed from saccharose and galactose, the latter originating in the decomposition of pectic substances, possibly by the action of an anti-emulsin.

In presence of saccharose and invert sugar, raffinose may be determined quantitatively by the optical method described later (Saccharimetry), or by the method devised by Ofner (1907), who extracts the whole of the raffinose with pure methyl alcohol, evaporates the alcohol, hydrolyses the remaining syrup for 3 hours on the water-bath with 3 per cent. sulphuric acid, and then precipitates the galactose as methylphenylhydrazone, which is quite insoluble and can be easily weighed ; the corresponding weight of raffinose can then be calculated. An exact determination of raffinose in sugar, which almost always contains less than 0·5 per cent. of it, is very difficult. The presence of raffinose in small proportion in saccharose is regarded as probable if the ratio between *non-sugar* and ash is less than 1·5.

INDUSTRIAL PREPARATION OF SACCHAROSE [1]

Saccharose is contained in varying quantity (5 to 20 per cent.) in different vegetable organisms. For instance, the sugar-cane (*Saccharum officinarum*) gives 15 to 20 per cent. ; the beetroot (*Beta vulgaris*), 7 to 17 per cent. ; *Sorghum*

[1] History of Beet-sugar. The first saccharine material worked and utilised by man as food was probably honey. The sugar-cane was known to the ancient Chinese, the Indians, and also the Persians and Arabs two hundred years before Christ and only later was it introduced into Egypt, Greece, and Sicily ; the medicine-men of this epoch employed cane-juice and honey as medicine. In the seventh century sugar in the solid form was an article of commerce, and in the eighth century the Persians extracted it from the sugar-cane and prepared it in cakes ; after the ninth century, the cultivation of the cane was extended by the Arabs to Egypt, Syria, Crete, Sicily, and Spain. In the fifteenth century, the Portuguese introduced the culture into Madeira and Brazil, while the Spaniards carried it to the East Indies and the Canary Islands, and the Dutch to Java and Guiana. At the present time the sugar-cane is largely cultivated in Cuba, Java, Manila, Martinique, Jamaica, Louisiana, Brazil, Peru, China, Japan, India, Egypt, and part of Australasia. In Europe it is grown to a small extent only in Spain.

In 1806, when France and the allied nations established the Continental blockade against England (lasting

saccharatum, 7 to 12 per cent.; the pineapple, 11 per cent.; strawberries, 5 to 6 per cent.; maize stems, sugar maple, &c., also contain small proportions of saccharose. Most sweet vegetable juices, however, contain glucose (grape-sugar) and levulose. The plants employed industrially for the extraction of sugar are the maple, sugar-cane, and beetroot. Unsuccessful attempts have been made with maize stems, which contain as much as 14 per cent. of sugar when the unripe heads are cut; but the sugar extracted sometimes contains 12 per cent. of invert sugar and other impurities.

I. **ACER SACCHARINUM NIGRUM** (**Sugar Maple**), which is largely cultivated in North America, is a tree requiring about 20 years to attain its maximum height of more than 9 metres and diameter of bole of 80 cm. In February, March, and April, three holes are made at different points (east, south, and west) with an iron borer; these holes penetrate to a depth of 1 cm., so as to pierce the bark, and are about 40 cm. from the ground. Into each hole is placed a hollow elder stem, which discharges the juice during a period of 5 to 6 weeks. The following year the holes are made on the other side of the trunk. In this way a maple yields 120 to 130 litres of juice containing about 3 kilos of sugar. The juice must be worked up each day, as it soon undergoes alteration; the method of treatment is similar to that used with beet-juice.

In 1880 North America produced 54,000 quintals of maple-sugar, while in 1904 the output amounted to 120,000 quintals.

II. **THE SUGAR-CANE** is the principal source of Colonial sugar.

It is a plant (*Saccharum officinarum*, Fig. 286) which has been cultivated from the most remote times in India, Persia, and Arabia, whence it passed into Egypt and Greece. At the time of the Normans it was cultivated in Sicily, and from there it was introduced in 1420 into Portugal and Spain, and thence into the West Indies; the Dutch carried it to the East Indies, where its development was very rapid. At the present time it is cultivated most widely in Cuba, Porto Rico, San Domingo, Havana, Brazil, and the East Indies (Bengal, Java, and the Philippines). In Mexico 450 quintals of cane per hectare are obtained, but the culture is primitive and the industry rudimentary. In Java a hectare of land yielded 680 quintals of cane in 1893 and an average of more than 1020 quintals in 1910. At Hawaii the yield was 600 quintals in 1895 and 835 in 1910. At Cuba as much as 1250 quintals per hectare are obtained, but even this amount, and also the 10 per cent. yield of sugar, might be still further increased.

The plantations are made with shoots from the living plant (obtained from seed), these being placed about 1 metre apart and weeded after 4 to 5 months. The cane begins

until 1814) and the supply of colonial sugar furnished by England to the whole of Europe hence failed, attempts were made to discover a substitute for cane-sugar.

As early as 1705 the French agriculturist, Olivier de Serres, had observed that the beet contained a considerable proportion of sugar, and in 1747 the Berlin pharmacist, Sigismund Marggraf, attempted the extraction of the sugar, obtaining a yield of 6 per cent; but at that time it could not compete with the much cheaper colonial sugar. Carl Achard, a pupil of Marggraf, after twenty years of experimental work on the selection of the best qualities of beet, &c., erected a factory for the manufacture of beet-sugar at Kunern, in Silesia (1801). But it was not found possible to extract more than 3 per cent. of crystalline sugar, which did not cover the expenses, so that the factory was closed. Achard, however, continued to perfect his process, and when the Continental blockade produced in 1811 a tenfold increase in the price of sugar, several beet-sugar factories were started in Germany; but these were still so imperfect that they were obliged to suspend operations when the blockade ceased. At this same time Napoleon I induced the most eminent scientific and technical men in France to apply themselves to this problem, and the extraction processes were rapidly improved, machines being devised for rasping and pressing the beets. With the introduction of the use of steam for concentrating the juices and of granulated bone-black for decoloration, beet-sugar began to compete seriously with colonial sugar, even after the raising of the blockade. In 1828 there were indeed 58 large and flourishing factories in France, producing annually 300,000 quintals of sugar. Napoleon I had distributed in prizes to encourage this industry the sum of £40,000 and had himself erected four factories and brought 32,000 hectares of land under beet cultivation.

In Germany the sugar industry was started again in about 1836, especially in the neighbourhood of Magdeburg, where a fortunate choice was made in the quality of beet employed, the lot of the agriculturist—at that time depressed owing to poor grain crops—being thus greatly ameliorated. The further development of this industry was favoured by protective duties imposed by the Government, in France—until a few years ago—and in Germany and Austria, where the prosperity of the sugar factories is continually increasing. The industry then developed in Belgium and Russia, while in Italy it was initiated only towards the end of the last century. In England the cultivation of the sugar-beet has been attempted, apparently with success, on a small scale only during recent years.

In 1855 the world's production of beet-sugar already amounted to 1,500,000 tons, and in 1900 Central Europe alone produced 8,500,000 tons. During the same lapse of time the output of cane-sugar increased only from $1\frac{1}{4}$ to $2\frac{1}{2}$ millions of tons.

to sprout in 12 months and requires a further 6 months to mature, when it has a yellowish colour and is 3 to 6 metres high and 4 to 6 cm. in diameter ; it sometimes reaches a weight of 9 kilos.

The stem and roots of each plant will yield cane for twenty consecutive years without renewal. The negro labourers remove the head (used for cattle-food) from the cane with a blow from a scythe, and with another sever the cane at the base ; the leaves (used for thatching) are then removed and the cane worked up each day, as it rapidly ferments if left in heaps. The omnivorous ant is the enemy most feared by the planter. At one time the bundles of cane were crushed in a primitive mill formed of three vertical cylindrical tree-trunks, shod with iron and worked by water-wheels or horses. But nowadays use is made of three horizontal cylinders, the distances between which can be regulated so as to vary the pressure (Fig. 287).

FIG. 286.

The liquid thus expressed is termed *raw juice*, and the woody residue *bagasse* or *megass*. After the cane has been pressed, it is moistened with water and again pressed (it contains then 4 per cent. of sugar and 45 per cent. of water), and then dried and burnt as fuel. In Mexico bagasse and the leaves of Henequen plants are now used for the manufacture of spirit. The total juice, including that from the second pressing, forms about 90 per cent. of the weight of the cane and contains 15 to 19 per cent. of sugar. In the East Indies, owing to irrational methods of working, more than one-half of the sugar is lost, whilst in Brazil, where improved processes are in use, more than 60 per cent. of pure sugar is obtained.[1] In North America the diffusion process has been introduced, and the loss of sugar reduced to less than 20 per cent. ; diffusion has also been tried in Brazil, but was abandoned owing to its expense, especially as regards fuel. Treatment of the fresh juice with a considerable amount of sulphur dioxide is often employed to prevent the ready fermentation which otherwise occurs. Attempts have also been made to decolorise with sodium hydrosulphite.

[1] The following information has been furnished by Alberto Bianchi, who has visited various cane-sugar factories in South America. The most important centres in South America for the production of the sugar-cane are: in Brazil, the States of Pernambuco, Bahia, Rio de Janeiro, and San Paulo, and, in a less degree, Maccio and Maranhao ; in Argentine, much cane-sugar is produced in the northern provinces, especially in Tucuman. The varieties of cane most widely grown in Brazil are *cana manteiga* and *cana preta*, which have been imported from Java and Haiti and yield from 10 to 17 per cent. of crystallisable sugar. The works are erected in the plantations, and the more primitive ones, in which the juice is still concentrated under the ordinary pressure, are called *Engenhos*, whilst those furnished with modern machinery and multiple-effect vacuum plant are termed *Usinas*

In the *Engenhos*, the broken cane is crushed between wooden rollers worked by oxen or horses. When the juice is not defecated, it is concentrated in large copper pans heated by direct fire, and is then left to crystallise in wooden vessels, the molasses being subsequently decanted off and the crystalline mass placed to drain in barrels with perforated bottoms. When defecation is employed, the juice is boiled with lime and skimmed several times, the defecated juice then passing into a series of two or three pans, each lower than the preceding one ; in the last of these the desired concentration is attained. The sugar thus obtained is always moist, owing to the residual molasses, and varies in colour from yellow to brownish black ; the yield is less than 6 per cent.

In the *Usinas*, where the yield may amount to 10 to 11 per cent. (by the wet process, or 7 to 9 per cent. by the dry process, or 6 per cent. when the cane is pressed in a single pair of rolls), the canes are pressed between

Even recently cane-sugar constituted about one-half of the total sugar produced, but it is nearly all consumed where grown in a more or less refined condition, whilst a very large trade is done in beet-sugar in a highly refined form, and in some cases this sugar competes with cane-sugar in districts where the latter is produced. The output of cane-sugar in Cuba alone was 700,000 tons in 1898 and 1,050,000 in 1904. In order to encourage the cultivation of the sugar-cane, the United States Government have instituted a system of bounties (as much as 11*s.* per quintal), and in 1910 paid £13,800,000 in this way; in addition to this there is a protective duty of 24*s.* per quintal on the sugar, this being paid by the consumer. In the East Indies the production increased to 2,166,000 tons in 1904. (The European output of beet-sugar is about 8,000,000 tons per annum.)

Cane-sugar molasses is of value owing to its agreeable flavour and smell, and it is therefore converted, by fermentation and distillation, into *rum*, that of Jamaica being especially renowned.

III. The **BEETROOT** was formerly an annual, but became changed by selection into a biennial, giving flowers and fruit (or seeds) only in the second year. Different varieties of *Beta vulgaris* or *Beta maritima* (Linnæus) are now grown. The original wild varieties contained only 5 to 6 per cent. of sugar, but after careful and repeated selection during a period of 25 years, varieties have been obtained which, under the most favourable conditions, contain as much as 18 per cent. of sugar.[1]

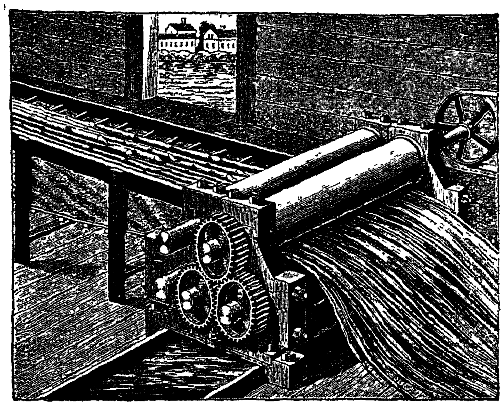


FIG. 287.

Nearly all of the best varieties now cultivated are derived from the Klein-Wanzleben. The shape of the root is of considerable importance. Thus, the rounder beets are generally rich in sugar but give a small crop; roots of oblong and swollen form crop well but are poor in sugar; whilst fusiform roots which are not too smooth and have little top and

three pairs of double rollers by hydraulic pressure, poorer juice (wet process) being gradually sprayed on to the partially pressed cane; the pressed cane is used as fuel. The juice, with a density of 5° to 10° Bé, is pumped to the sulphitation tanks (sulphur dioxide or calcium bisulphite is used; but this is not done in all factories) and thence passes to copper vessels with spherical bottoms and holding 2000 to 4000 litres. In these it is defecated with milk of lime, being heated by steam coils and skimmed once or twice. After carbonation, the juice is transferred to other vessels of about the same size as the former ones and placed at a lower level; in these it is again boiled and skimmed. It is next removed to the depositing tanks and, after some hours, is pumped to the triple effect vacuum concentrators, from which it passes at 23° to 26° Bé. to copper boilers of 2000 to 4000 litres capacity (clarifiers), where it is boiled by means of steam coils for about half an hour—until it ceases to form scum (which is removed). The juice is next boiled in a vacuum apparatus, in which crystallisation commences; the subsequent treatment and refining of the sugar are carried out as in beet-sugar factories (*see later*).

In many factories, the yield of white, first-jet sugar is increased by decolorising the juice, not by sulphitation, but by the addition of *blankite* (*sodium hydrosulphite*) in the proportion of 300 to 500 grms. per ton of sugar; this is added partly to the clarifier and partly to the concentration vessel.

It is calculated that the cost price of cane-sugar in the factory, without reckoning interest on capital, is 15*s.* per quintal in Java, 18*s.* in Cuba, and 25*s.* in Hawaii.

[1] Achard himself recognised varieties of the beet best adapted for the manufacture of sugar, but it was Vilmorin, in France, who in 1856 rationally selected the first variety rich in sugar (*Vilmorin's white*) by repeated reproduction of the roots with the highest saccharine content; this he arrived at by immersing the roots in saline solutions of different concentrations so as to determine their specific gravities, from which he deduced the content of sugar. Later, however, Scheibler showed that there is not always proportionality between the specific gravity and saccharine value.

In Germany, more rigorous methods of selection were introduced by Rabbethge and Giesecke (1862), who analysed selected beets cut into portions and determined, not only the richness in sugar, but also the purity of the juice polarimetrically. Kuhn then improved the selection still further by microscopic examination of the seeds.

Choice of seed is of great importance and seed should be obtained only from reliable firms; a saving of a few shillings in buying seed sometimes involves serious losses.

Special preparation of the seed (shelling, impregnation, &c.) does not appear to have any practical value, but, on the other hand, Briem (1910) states that repeated selection and adaptation to the new intensive culture methods is able to produce in 20 years an increase in the mean saccharine content from 14 to 19 per cent., besides an increase in the weight of the beets owing to the roots becoming accustomed to more energetic fertilisers.

There are now numerous varieties of beetroot known by the names of their producers or of the places where they were first selected. Among such varieties the best are the Klein-Wanzleben, Dippe, Kuhn, Braune, Vilmorin, &c.; these can be distinguished, although not always readily, by the shape of the roots and leaves and by the saccharine content.

tail (waste products of the sugar factory) are the ones preferred by the agriculturists and manufacturers (*see* Fig. 288).

Value attaches, besides to the shape, also to the specific gravity, and still more to the sugar-content. Fig. 289 shows the saccharine content of the various zones composing the beetroot. It will be seen that the richness in sugar diminishes from the centre to the periphery, and especially to the top and tail, which also give the more impure juices.

Beetroots for fodder or for domestic purposes are yellow or red, but those selected for sugar are white, and any variegation or colouring with the original tint indicates faulty selection and degeneration or reversion to the primitive type. Roots with few leaves or with long stems are poor in sugar, and denote that the soil is of a character not adapted to their cultivation.[1]

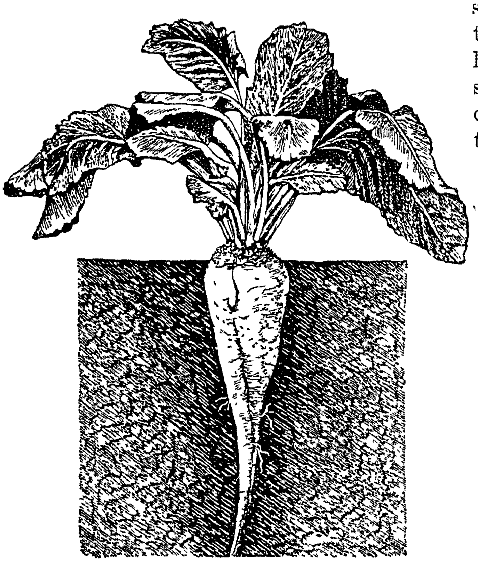


Fig. 288.

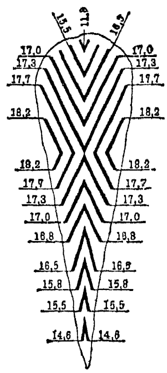


Fig. 289.

The proportions of the principal components of the beetroot vary between the following limits (percentages): water, 75 to 86; sugar, 9 to 18; cellulose and lignin, 0·8 to 2·5; nitrogenous (protein and amino-) substances, 0·8 to 3; fat, 0·2 to 0·5; mineral matter (potassium and other salts), 0·2 to 2. Other and less important components of the beet

[1] **Beet Cultivation.** Sandy or very compact (clayey) soils are not suited to the growing of beet. The most suitable are medium soils which can be worked to a considerable depth (35 cm) in the *summer* months. In Italy, where the rain is not so well distributed as in Central Europe, it is necessary to sow early in order to avoid the excessively dry season.

Fertilisation should be abundant, since from a hectare of soil beets remove annually as much as 120 kilos of potash (K_2O) and 52 of phosphoric anhydride. Stable manure serves well as the fundamental fertiliser, but the sugar manufacturers require the farmers to apply it in the summer, during tilling, and not in the spring; any large use of nitrogenous manures is inadvisable. According to Stoklasa (1910), the most suitable manuring for beet is obtained by a rational application of nitragin (*see* vol. i, p. 302) As supplementary fertilisers, superphosphate (about 4 quintals per hectare) and sodium nitrate (1 to 1 5 quintal per hectare) are largely used. To ascertain if a soil requires also potash (kainit, carnallite, chloride, &c), the presence or absence of potassium salts in the drainage water is determined by analysis. In general, however, 1 5 to 2 quintals of potash fertiliser are employed per hectare, since beet takes about 160 kilos of potash from the soil every year. But in all cases these chemical fertilisers should be administered at intervals prior to May, as otherwise the sugar manufacturer may refuse the roots owing to the excessive amount of salts in the juice; not only is the latter rendered more impure but the salts, especially chlorides, prevent the crystallisation of part of the sugar. Irrigation is inadvisable and, in some cases, is prohibited. A large area of soil in the province of Magdeburg became infertile owing to the repeated cultivation of beet, but it recovered its original fertility after the discovery of the deposits of potassium salts at Stassfurt.

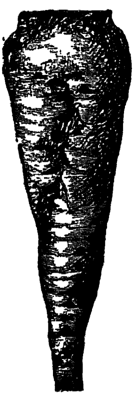


Fig. 290.

In sowing (which is carried out between the beginning of March and the middle of April, with a drilling machine giving rows 35 to 40 cm. apart), excess of seed is always used, so that after the plants have begun to grow, 15 to 16 per sq. metre may remain. The roots then attain an average weight of 500 to 600 grms. (isolated beets sometimes weigh 4 to 5 kilos) and, under favourable conditions, a hectare yields 300 to 400 quintals of beet (in Ferrarese as much as 600 quintals are obtained, while in the other Italian provinces the average is about 300). If sowing is delayed too long, the roots do not mature well but remain acid and give very impure juice.

Growth begins 5 or 6 days after sowing, and when the seedlings are a few centimetres high women and children proceed to thin them out with ordinary hoes, just as is done with maize Later on, the ground is hoed several times to remove weeds and to keep the soil sweeter in the warm weather.

are: glucose, raffinose, organic acids (oxalic, malic, tartaric, citric, malonic, succinic, glutaric, gluconic, tricarballylic), amido- and amino-compounds (leucine, asparagine, betaine, tyrosine), gums, pectic matters, coniferin, &c.

The value of the beets was formerly arrived at by measuring the density of the juice with the Brix densimeter, but the results varied considerably with different varieties of beet and also from other causes. It is usual nowadays to determine the quantity of the sugar in the juice by means of the polarimeter (*e.g.* the Soleil-Ventzke-Scheibler or, better, the three-field instrument of Schmidt and Haensch; *see later*).

A sample of the beets arriving at the factory is obtained by allowing fifty to fall into a basket while the waggon is being unloaded, placing the fifty in a row and taking the alternate ones, repeating this operation on the 25, and of the 12 thus obtained choosing one small, one medium, and one large. From each of these three, a longitudinal portion is removed by means of the *Pellet rasp*, which gives directly a homogeneous paste, the juice being expressed from this by a hand-press (Fig. 291). Of the well-mixed juice, 26·048 grms. (the normal weight of the polarimeter; *see later*) are introduced into a graduated 100 c.c. flask, which is filled to the extent of about two-thirds with water and 5 c.c. of basic lead acetate solution; after the flask has been well shaken, one or two drops of ether are added to remove the froth, and the solution made up to volume with water, filtered through a dry filter, and read in the polarimeter in a 20 cm. tube (*see later*).

FIG. 291.

At the same time the Brix densimeter is used to determine the density, so that the quantity of non-saccharine substance (*non-sugar*) and the purity may be estimated. The quotient of purity is obtained by multiplying by 100 the ratio between the true sugar-content and that (greater) indicated by the densimeter.

The sugar may also be determined by direct extraction for 2 hours in a Soxhlet apparatus (*see* p. 374) of 26·048 grms. of the beet pulp, mixed with 3 c.c. of basic lead acetate solution, with 75 c.c. of 90 per cent. alcohol. The alcoholic sugar solution is cooled, made up to 100 c.c. with water, filtered through a dry filter, and polarised in a 20-cm. tube. A very sensitive test for indicating if all the sugar has been extracted from the pulp in

If the season is a wet one, the roots are late in maturing (end of September or, in Germany, end of October) and are poor in sugar, and have soft tissues which readily give up their juice. In Italy, harvesting takes place normally in August, or, in some cases, earlier than this.

When the beets are ripe the leaves dry somewhat and, if the roots are not dug immediately, in warm climates new leaves may be formed to the detriment of the sugar-content. On this account the factories are arranged so that they can deal in a short time with the whole of the crop. The harvesting is carried out in several portions, since the manufacturer requires roots not more than 3 to 4 days old, alteration occurring on storing.

Beets which have flowered prematurely (in a cold spring or a very dry season) are hard and difficult to exhaust and the manufacturer demands that such plants should be pulled up or, at least, that the flowering shoots should be suppressed. Putrefaction of the roots, besides injuring the quality and quantity of the crop, sometimes damages a large part of the beet. Among the various insects injurious to the beet is one which destroys the feeble plants.

In soil which is worked insufficiently and not deep enough, or is treated too late with stable manure, the beets tend to form bifurcated roots and so give an increased amount of waste, which is not paid for by the manufacturer.

In Italy, contracts are made on the basis of 1*s.* 7*d.* to 2*s.* per quintal for beets without roots and tops (Fig. 290), 1*s.* 9*d.* being paid if they are delivered in the first half of August and sometimes only 1*s.* 4*d.* if in October. Some Italian sugar factories have succeeded in making contracts on the basis of the percentage of sugar present, as is often done in other countries.

The manufacturer usually deducts 5 per cent. or, in exceptional cases, more, on account of admixed stones, soil, &c. As a rule, roots containing less than 9 per cent. of sugar are not accepted.

A few years ago the proposal was made that the dried leaves of the beet should be utilised as fodder, of which Germany alone could produce £8,000,000 worth annually.

the two hours consists in adding to a couple of drops of the last drainings from the Soxhlet apparatus 2 c.c. of water and 5 drops of a fresh 20 per cent. alcoholic α-naphthol solution, and then pouring 10 c.c. of concentrated sulphuric acid (free from nitric acid) carefully down the side of the test-tube; in presence of sugar, a violet ring (not green, yellow, or reddish) forms at the surface of separation of the two liquids (*see also* p. 441).

EXTRACTION OF THE SUGAR FROM THE BEET. After many and varied technical and economic difficulties had been overcome, the beet-sugar industry became firmly established and has during the past quarter of a century assumed great importance, not only on account of its magnitude, but also owing to its technical perfection, which makes it a model of what a great modern chemical industry should be.[1]

We shall now follow shortly the whole of the working of a rational sugar factory as far as the refining of the crude sugar and the utilisation of the molasses.

(1) **Storing and Washing of the Beets.** When the beets are topped and freed from soil and stones they are weighed (1 cu. metre weighs 500 to 600 kilos) and then discharged under long sheds (Fig. 292) with pavements sloping to a longitudinal channel, *A*, which is covered with movable boards or gratings and has water flowing through it (Fig. 293). The beets should not be kept long in these silos, as after a few days loss of sugar occurs. The sugar-works are, however, designed to deal with a large quantity of beets every day (4000 to 8000 quintals), so that the whole of the year's crop may be worked up in 50 to

[1] **History of the Technical Development of the Beet-sugar Industry.** In his earliest industrial trials, Achard (1786) extracted the sugar by boiling the beets in water, expressing the juice, concentrating this to a syrupy consistency, and allowing to crystallise in the cold. In France, to facilitate the separation of the juice, the beets were disintegrated by means of rasps which converted them into a fine paste, this being squeezed in screw presses and later in far more powerful hydraulic presses. The juice was then defecated with lime and, after neutralisation with sulphuric acid, concentrated in copper pans. On cooling, crude crystalline sugar was obtained.

In Germany, however, the juice was first treated with sulphuric acid and, after a short rest, neutralised with chalk, heated with lime and filtered. The saccharine solution was concentrated by direct-fire heat and decolorised with animal charcoal, albumin, or even blood. The crystallisation was carried out in wide, shallow pans.

In some places use was made of the old Colonial process of concentrating the juice until, on cooling, it gave a dense mass of crystals which was introduced into inverted conical moulds. The point of the cone was closed by a plug, which was then removed to allow the liquid to flow away, the sugar-loaf being subsequently removed.

Only later, after a proposal made by Weinrich, was the lime used for defecating the juice neutralised by carbon dioxide instead of by sulphuric acid, inversion of the sugar being avoided and improved defecation obtained. At the outset, the carbon dioxide was prepared by the costly method of treating calcium carbonate with hydrochloric acid, but later it was obtained from the combustion of coal, and finally by heating chalk in suitable retorts or furnaces, the residual lime being also utilisable.

Further improvements were made also in the rasps, as the living cells of the beet, being coated inside with protoplasm impermeable to the cold saccharine liquid, do not allow the sugar to exude; it is hence necessary to rupture the cells as completely as possible.

A considerable advance was made in 1836 by Pelleton, who introduced *cold maceration* of the rasped beet with a counter-current of water. This systematic exhaustion was improved by Schutzenbach, who arranged the vessels of beet-pulp in steps, the water entering the top vessel and being collected after it leaves the lowest one and then pumped to the top, and so on; the pulp was exhausted with fresh water and the exhausted pulp replaced by a fresh supply. It was necessary to attend to the cleanliness of the plant in order to avoid the development of micro-organisms capable of inverting the sugar. In 1837 Schützenbach suggested the preliminary drying of the pulp and its extraction with water at 90°, which renders permeable those cells not broken by the rasp. Fesca and Schrottler, on the other hand, centrifuged the fresh pulp directly—just as is now done with the crystallised sugar (*see later*)—and subsequently sparged the pulp with cold water in the centrifuge itself so as to obtain more perfect exhaustion. But all these processes were too expensive and did not give complete extraction of the sugar, much of which was still lost.

It was only after 1864, when the *diffusion process* was devised, that complete extraction of the sugar became possible (*see above and later*).

Defecation was also facilitated by separating the organic impurities precipitated by the lime, not with slow and cumbrous bag-filters, but by the filter-press invented by Needham in 1828, improved by Kite and employed in defecating by Daněk in 1862. By this means, working was hastened and cheapened, and further improvement was made when the filter-press was so modified as to permit of the washing and exhaustion of the calcium carbonate with hot water in the press itself.

The application of animal charcoal (bone-black) filters, which had been proposed for other industries by Figuier in 1811, proved of considerable advantage in the clarification and decolorisation. The bone-black readily fixes the colouring-matters and the chalk, but does not retain the sugar. As it becomes enriched in calcium carbonate, however, it loses its decolorising property and hence required frequent renewal at great expense. Subsequently the activity of the charcoal was restored by treatment with dilute hydrochloric acid to eliminate the carbonates and then fermenting at a suitable temperature and with a suitable proportion of moisture, in order to destroy much of the organic matter; the charcoal was then washed thoroughly with water and dried in long iron tubes heated to low redness in a furnace (*see* p. 471). A factory with a capacity of 4000 quintals of beet per day should have at its disposal 6000 quintals of animal black throughout the whole season. The cost of this is considerable, and during recent years these filters are being dispensed with in the sugar factory, methods of defecation being improved and the filters used only in the refinery.

The sugar solutions were, at one time, evaporated by direct-fire heat, a total of 40 kilos of coal being consumed per quintal of beets. In 1828, Moulfarine and Decquer in France introduced the use of steam-coils, and in 1840 the employment of the Hovard vacuum evaporator reduced the consumption of coal to 25 kilos. Since 1852, simple or multiple-effect vacuum evaporators (Rillieux) have come into use and these, after many improvements, have still further diminished the amount of coal required until nowadays it is only 7 to 8 kilos.

60 days. In order to transport the beets to the place where they are first required, the covering of the water-channel is gradually removed so that the roots fall into the water, which carries them half floating to the principal elevator, *B*, this separating the mud and water and delivering the beets to the washer, *C*.

The elevator may consist of a large wheel fitted with a number of perforated plates (Fig. 294) or of an inclined screw having a perforated sieve-plate at *G* (Fig. 295).

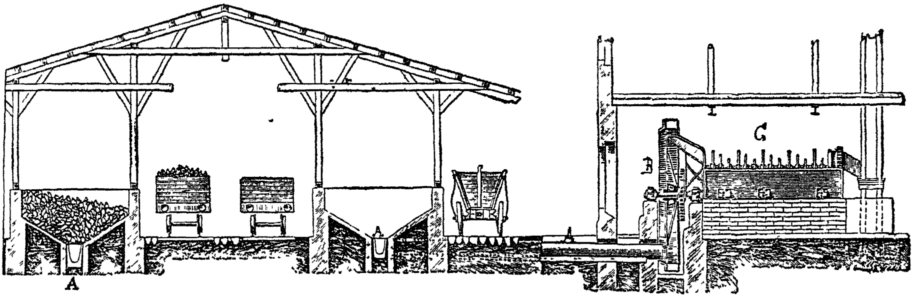


FIG. 292.

Nowadays, however, the beets are conveniently raised by applying the principle of the Mammoth pump (*see* vol. i, p. 265), which also admits of a more complete washing.

The washing is carried out in iron or concrete vessels, 4 to 6 metres long and 1·5 to 2 metres wide, furnished with a longitudinal bladed spindle by which the roots are beaten in the water and transferred to the other end of the washer; on the bottom are indentations or an inclined plane on which any stones collect, to be discharged from the orifices, *D* and *E* (Fig. 295).

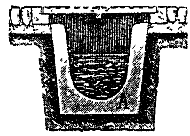


FIG. 293.

In 24 hours such a washer can treat as many as 5000 quintals of beet, about the same number of hectolitres of water being consumed.

From the washer the beets fall into basins, whence they are raised by a large vertical elevator to a higher part of the factory and dropped into a double automatic weighing machine, which discharges 50 to 100 kilos or more at a time into the *cutter* or *slicer;* in the latter they are reduced to thin slices suitable for extraction by the diffusion process. The slicing machine is formed of a vertical chamber, *A* (Fig. 296), which receives the roots,

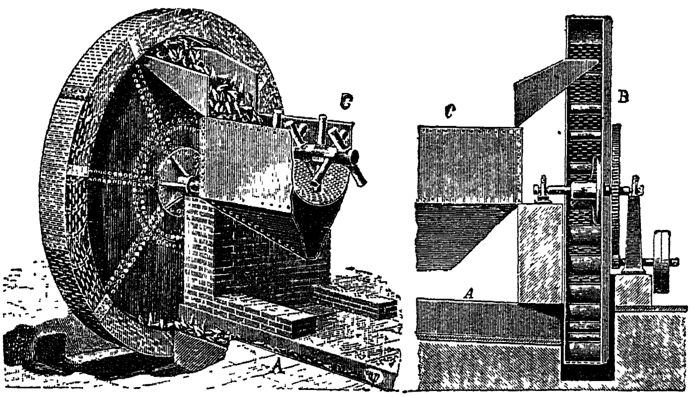


FIG. 294.

and the base of which consists of a circular cast-iron plate, *C*, rotated by means of a vertical shaft and furnished with 10 to 15 rectangular apertures, *a a* (*see* plan and section, Fig. 297). In these apertures fit cast-iron frames carrying a series of undulating cutting blades which form knives of various shapes (Fig. 298). The beets at the bottom of the chamber are forced by those above against the rotating knives and so sliced. The form of these slicers varies somewhat in different factories, and in some cases the revolving plate has a diameter

of 1·2 to 1·5 metre and a velocity of 100 to 140 turns per minute. The beet-chamber is about 1·5 metre high.

At one time use was made of knives with several superposed blades at various distances apart, but these give smooth slices or prisms (if cut longitudinally) which readily adhered one to the other and hence presented a diminished surface in the subsequent diffusion operations. Good results are, however, obtained with those having a zig-zag section (Fig. 299) and giving slices having the form of triangular channels; sometimes a blade is placed at the apex of each angle, so as to prevent the formation of wide slices. The side of the triangle in the blades is 6 to 7 mm., and the thickness of the slices is regulated by the height of the knives above the plate, *a* (Fig. 298).

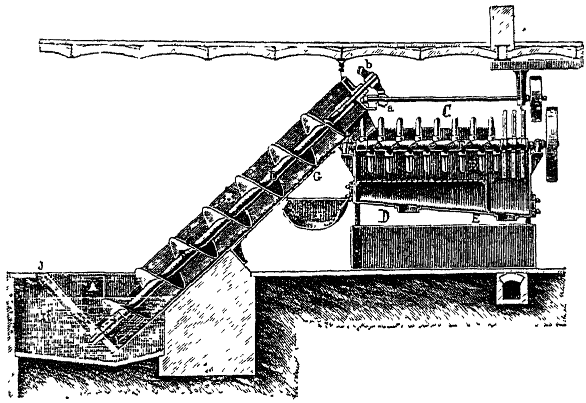


FIG. 295.

Centrifugal slicing machines are also used, these having knives fixed to the inner periphery of the vertical drum, which receives the roots and projects them against the blades. These machines give a greater output and uniform working, the knives being replaceable when in action. The knives usually wear rapidly, especially if stones occur in the interior or in indentations of the roots, and they should be changed frequently, as otherwise they do not cut clearly but tear, this resulting in slow extraction of the sugar in the diffusors. The knives are sharpened with triangular files or with suitable milling-cutters.

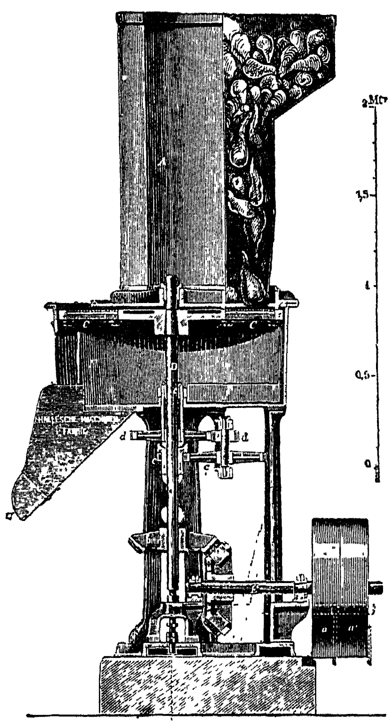


FIG. 296.

EXTRACTION OF SUGAR BY THE DIFFUSION PROCESS. In the note on p. 448 mention has already been made of the various steps made in the extraction of sugar from beets and of the diffusion process, which is now used and which presents marked advantages over earlier methods. The diffusion process is based on the general laws of osmosis (*see* vol. i, p. 77). If a solution of sugar (or salt or, in general, any crystalloid) is enclosed in a porous membrane immersed in water, the sugar molecules pass slowly through the membrane to the outside (exosmosis), while water passes from the outside to the inside (endosmosis). This process continues until the specific gravities of the sugar solutions inside and outside are identical (equal numbers of sugar molecules then pass through the membrane outwards and inwards); or, if it is required to remove all the sugar from the inside, the water outside is continually renewed. The same phenomenon is shown by the sugar-containing vegetable cells of the beet. The envelope of the cell functions as an osmotic membrane, although the sugar inside the cell and the walls of the latter also are coated with protoplasm which, at the ordinary temperature, prevents or greatly retards the osmotic flow.

But at a temperature of 70° osmosis takes place more readily through the saccharine cells of the beet, the protoplasm then coagulating and the walls becoming permeable to

the osmotic currents. Under these conditions the complete extraction of the sugar is possible (not more than 0·3 to 0·4 per cent. is left).

The first industrial application of this method was attempted in 1864 by Robert in the celebrated factory at Seelowitz (Moravia), and the results were so favourable that by 1867 about thirty factories had adopted it. It was then that the idea was evolved of cutting the beets into slices to facilitate the osmotic phenomena, the extraction being effected by systematic and continuous exhaustion in a series of cylindrical vessels containing the slices. Water at 70° enters the first cylinder, carries away part of the sugar, and then passes to the other cylinders in succession, until it reaches in the last the same density (about 10 to 12 per cent. of sugar) as the saccharine juice of the cells of the fresh beet. When the first cylinder is exhausted it is recharged with fresh slices and placed at the other end of the series. What was previously the second cylinder now receives the pure water and is hence exhausted, after which it is filled with fresh slices and made the last of the battery, and so on. In such manner the process becomes systematic and continuous, being carried on day and night during the whole of the campaign. The circulating water is brought to a temperature of 70° while passing from each cylinder to the next.

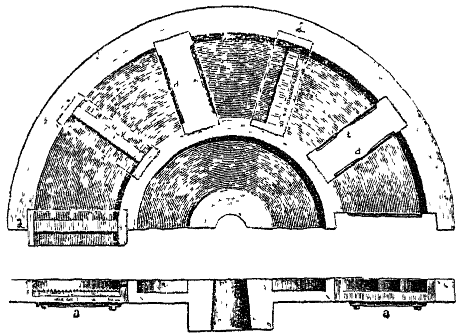


FIG. 297.

Diffusor Batteries. The diffusors are vertical iron cylinders with a capacity of 15 to 50 hectols. and a height double the diameter. They are furnished with an upper aperture for charging with the slices and one at the bottom or side for the discharge of the exhausted pulp.

They are arranged in batteries of 12 to 24 diffusors connected by pipes and valves, heating tubes being placed between. For a factory treating P quintals of beet per 24 hours, diffusors having capacities of $\frac{P}{100}$ hectols. each are now used.

The diffusors are often arranged in two parallel rows (Figs. 300, 301, 302), and if they are then discharged laterally the exhausted slices can be collected by means of a single

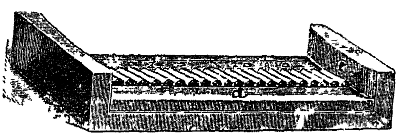


FIG. 298.

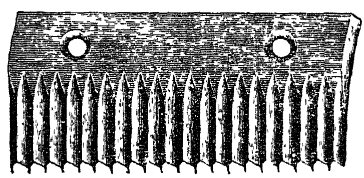


FIG. 299.

screw or travelling band, h, which carries them to the elevators, m; where they are discharged through an aperture in the base (Fig. 303), two channels with screws are used.

Sometimes the diffusors are placed in a ring, as is shown in section in Fig. 304 and in plan in Fig. 305. The diffusors are charged by means of suspended tubs coming from the slicing machine, or of an endless belt moving above them on rollers and flanked with a fixed plate forming an edge fitted with doors corresponding with the various diffusors. By opening a door and placing a plate diagonally on the belt, the slices are forced off the latter into a sloping channel and so into the diffusor; this operation is repeated until all the diffusors are full.

When the diffusors are arranged in a circular battery, the slicing machine (D, Fig. 304) is placed so that it commands the diffusors, which are charged by means of a shoot, E.

A perforated false bottom and an upper perforated disc in each diffusor prevent the penetration of the beet slices into the tubes that supply water or carry off the juice. To avoid accidents when operations are started, the tubes are provided with safety-valves

Air-cocks on the covers allow of the escape of the air displaced by the water entering the diffusors. Thermometers are inserted in the tubes to indicate the temperature of the water and of the circulating juice. There are tubes for cold water, transference of the juice, washing water, discharge of the water, steam for the heaters, and discharge of the juice.

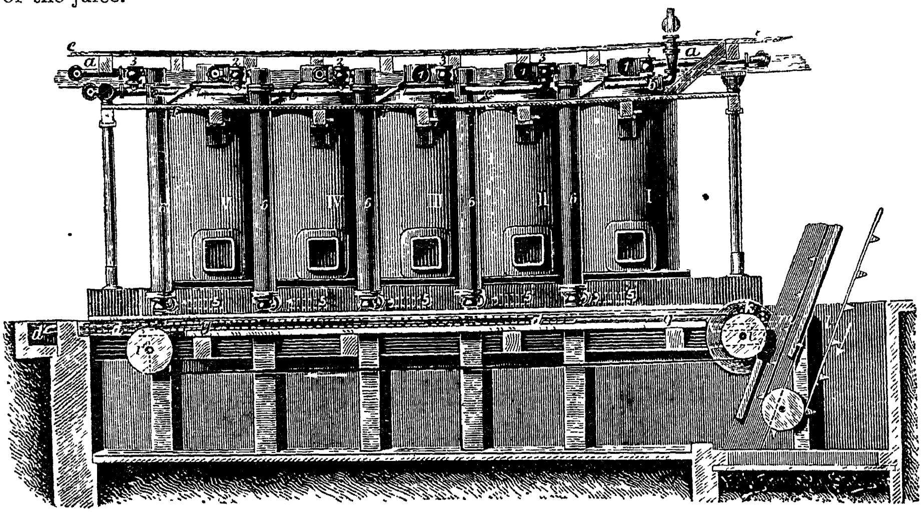


FIG. 300.

The *heaters* used to regulate the temperature of the circulating juices consist of a series of steam-pipes (*see* 6, Fig. 301) round which the juice passes. A less rational method of raising the temperature consists in blowing steam into the juice; this not only dilutes the juice but may cause caramelisation.

Water is supplied to the diffusor battery through two pipes which join just before the diffusor is reached; one of these comes from a cold-water cistern 8 to 10 metres above the level of the diffusors and the other from the boiler. Mixture of the hot and cold water in the proper proportions gives the temperature required for diffusion, this being at first about 35° and later 70° to 75°, to which it is brought by the heaters.[1]

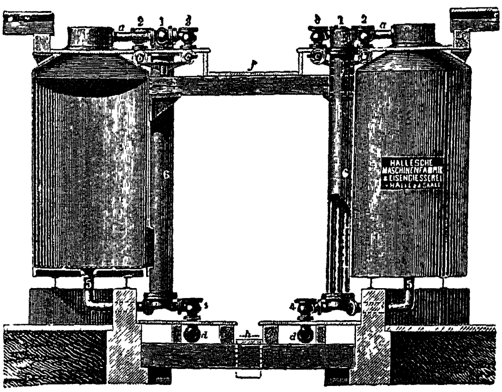


FIG. 301.

[1] **Method of Starting a Battery of Diffusors.** In the various tubes common to all the diffusors are inserted valves which admit of the communication of the tubes with each diffusor and also of the isolation of any diffusor from its two neighbours. The juice discharge pipe is furnished with a valve placed to the left hand of the upper pipe (*see* Diagram, Fig. 304) leading to the juice measurer and then to the collecting vessel. Assuming the battery to consist of 12 diffusors (in two parallel rows or in a ring), the first three are closed above and below, while the remaining ones are closed only at the bottom. Into the empty diffusor, I, water at 35° is passed through c, the air-cock, a, in the lid being left open; when I is full, the air-cock is closed and the juice-valve, c_2, the steam-valve of heater 1 (not shown in the figure) and the air-cock of diffusor II opened, II thus being filled with water at 50° (shown by the thermometers in the pipe by which the juice leaves the heater). When II is also full of water, the air-cock is closed and III then filled in a similar manner with water at 70°. While these operations are proceeding with the first three diffusors (containing no slices), the slicing machine is started and diffusor IV and the rest filled with slices. But as soon as IV is full, the slices are covered with the perforated disc and the lid closed, the air-cock, a_4, being left open. Then, on opening the taps, d_3 and d_4, of the juice-pipe, IV becomes filled from the bottom upwards with water at 75°, which first passes downwards through the heater 4. It is an advantage to introduce the liquid at the bottom of the diffusor, as the slices are thereby lifted and the air completely expelled. In diffusor IV the water begins to extract the sugar from the slices, and when the liquid has risen to the air-cock, a_4, this and also d_3 are closed, while the valves c_4, d_5, and a_5 are opened. By this means, since c is kept in communication with the water cistern at a head of about 10 metres, the water forces the liquid from I into II, and so into III, IV, and V, the course taken being I, 1, c_2, II, 2, c_3, III, 3, c_4, IV, 4, d_4

The amount of juice extracted normally by every diffusor is about 48 to 55 litres per hectolitre capacity of the diffusor (*i.e.* 100 to 110 per cent. of the weight of the beets, since

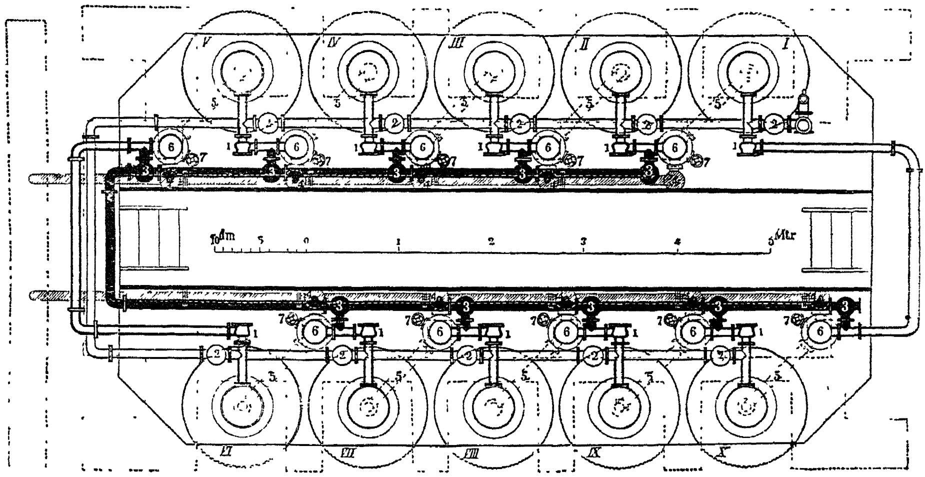


FIG. 302.

each hectolitre holds 50 to 55 kilos of slices). The amount of water necessary for complete diffusion (including washing water) is 1·2 to 1·5 times the weight of the beet (hence the water-tank should have a capacity at least as great as 3 or 4 of the diffusors).

Pressing and Drying the Pulp. The pulp (exhausted slices containing less than 0·5 per cent. of sugar) discharged from the diffusors is transported by a screw or endless band to an elevator which discharges it into the *pulp-press* (*M*, Fig. 305), where the water it contains (95 per cent.) is removed as completely as possible. Presses of various forms are used for this purpose.

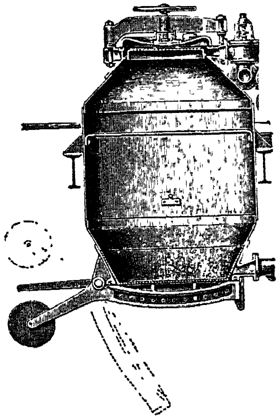


FIG. 303.

d_5, V. When the juice reaches a_5, the same operation is repeated, that is, a_5 and d_4 are closed and c_5, d_6, and a_6 opened, so that the juice is forced from the preceding cylinders into VI through 5, d_5, d_6, and 6, the temperature being kept at 70° to 75°.

The juice from VI is not passed into VII, but part of it is first discharged (*see later*) into the juice measurer (and thence into a reservoir) by opening the main valve, *M*, and keeping d_7 shut; when the amount in the measurer reaches a certain value, *M* is closed, d_7 opened and diffusor VII filled from below in the usual manner. In all these cases the pressure is supplied by the water in the raised cistern. When VII is full, before the juice is passed into VIII, part of it is discharged into the measurer through the valve, *M*, as before; these operations are repeated until the last diffusor is reached. When, however, IX is filled, it is advisable to discharge the water from diffusors I, II, and III, and to fill these with slices, so that, when the juice arrives at III, it is certain that the slices in IV (the first to be extracted) are exhausted; IV is then emptied and recharged immediately with fresh slices.

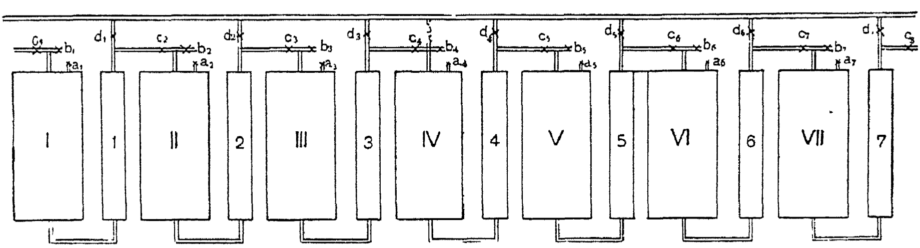


FIG. 304.

The juice is then passed from III to IV, while V is discharged and recharged, and so on. The working thus assumes its normal course. In case of accident, the workman regulating the taps immediately shuts off the steam and water, so as to prevent caramelisation of the juice and loss of sugar.

The temperature is 35° in the diffusor following that which receives the fresh water, then rises to 60°, and in the last diffusor (preceding that into which the water first passes) is 70° to 75°.

That of the Klusemann type consists of a vertical, revolving cone of perforated sheet-metal, *C* (Figs. 307, 308), fitted with oblique vanes and enclosed in a stationary cylinder, also perforated. The vanes, which are arranged helically alone the cone, compress the

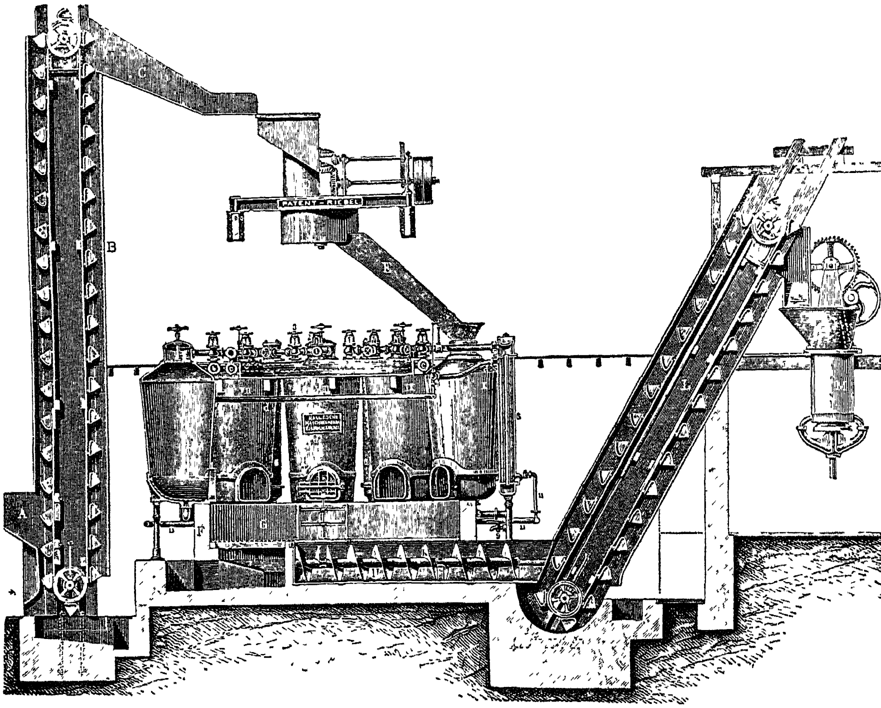


FIG. 305.

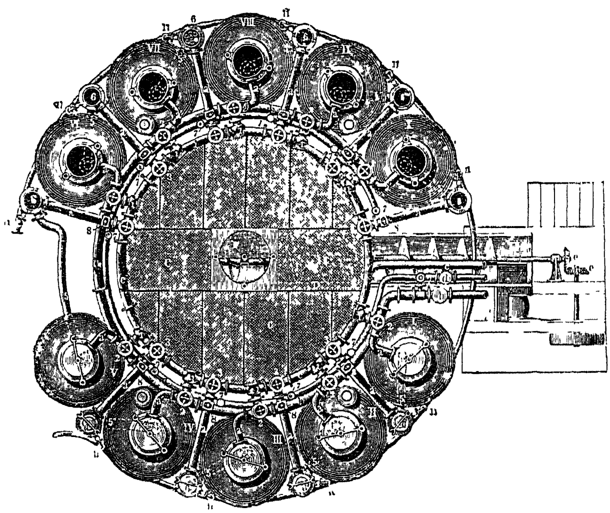


FIG. 306.

mass of pulp against the perforated cylinder and gradually move it downwards where the space becomes narrower, so that a considerable part of the water is squeezed out through the cone and cylinder, which are enclosed in a jacket, *E*; all the water is carried off by the tubes *F*, *G*, and *H*, while the pressed pulp is discharged through the annular orifice, *I*. An arrangement similar to this has also been combined with the pulp-elevator, which consists of an inclined screw, the pulp being thus raised and pressed at the same time.

The Klusemann press has been improved by Bergreen and others in order to diminish the amount of water left in the pulp. Each quintal of beet yields about 80 kilos of pressed pulp containing, on an average, 72 per cent. of water, 3 per cent. of ash, 1·8 per cent. of protein, 0·27 per cent. of fat, 6 per cent. of cellulose, and 17 per cent. of non-nitrogenous extractive matter.

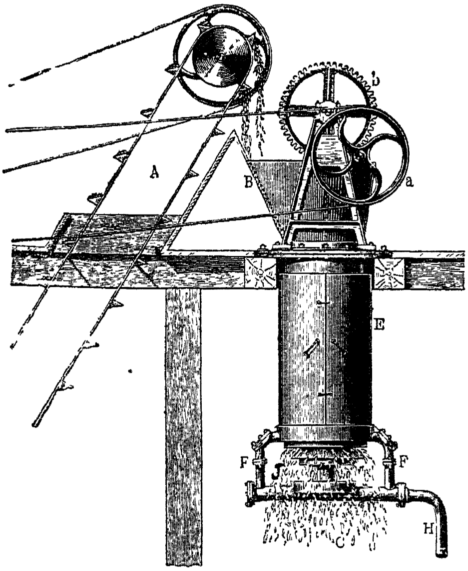


FIG. 307.

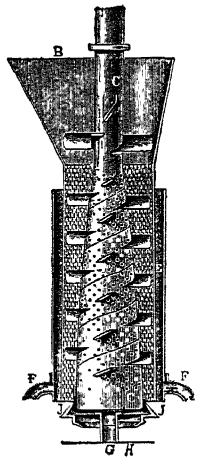


FIG. 308.

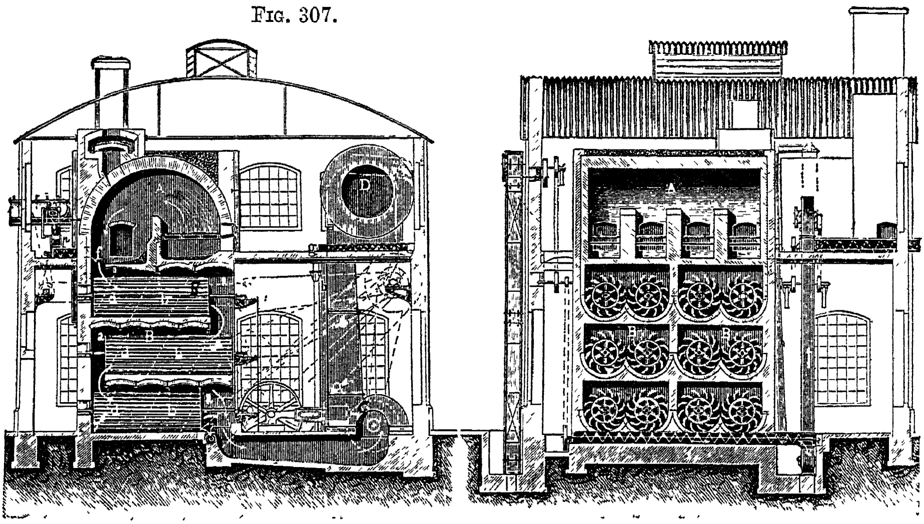


FIG. 309.

The pressed pulp is loaded directly on the farmers' waggons to be used as fodder, about 10*d*. per quintal being paid for it ; but part of it (30 per cent. of the amount of beets they supply to the factory) is given to them free of cost. If the pulp cannot be sold immediately, it is stored in silos until sold. But if this is done, it readily undergoes putrefactive fermentation, the gasogenic bacteria of which contaminate milk and cause inflation of cheese, so that in some countries, where fuel is not expensive, it is preferred to dry the pulp at once. It is known, too, that fresh pulp in silos loses as much as 40 per cent. of its solid matter, which is rendered soluble and volatile by bacteria, the sugar being converted almost completely into lactic acid.

Of the various types of apparatus for drying the pulp, that of Büttner and Meyer (*see* Fig. 309), which was devised in 1887–1888 and rapidly came into use in Germany,

France, Belgium, and Austria, gives good results. In 1898 sixty German factories were employing pulp-driers on this plan. The moist pulp is raised by means of an elevator, *p*, and dropped at *f* into an upper chamber, *B*, composed of four semi-cylindrical channels containing mixers revolving in opposite senses, which stir and lift the pulp and at the same time transport it to the mixers of the similar chamber below ; thence it passes to a third chamber. A current of air at 400° from a furnace enters *A* at *f* and is moved in the same direction as the pulp by the aspirator, *C*, which then forces it into the dust chamber, *D*, and thence to the shaft. The pulp should issue at a temperature of 110° so that moisture may not condense on it, and the supply of pulp is regulated so that the final proportion of water present is 12 to 14 per cent.

The composition of the *dry pulp* is as follows : 12 per cent. of water, 6·5 per cent. of ash, 8 per cent. of protein, 1·2 per cent. of fat, 18 per cent. of cellulose, and 55 per cent. of non-nitrogenous extractive substances (5 to 7 per cent. being sugar) ; it is sold in Italy at 6*s*. 6*d*. to 8*s*. per quintal. Recent tests made by Gorini (1911) show that the dry pulp is not sterile, and may hence be dangerous to milk during milking operations.

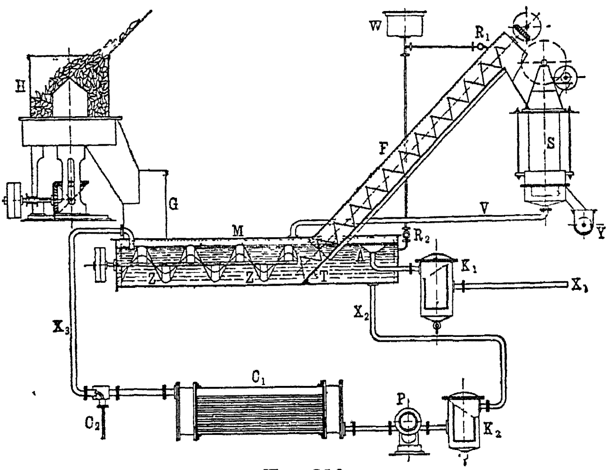


FIG. 310.

THE STEFFEN PROCESS. Some years ago Carl Steffen patented (Ger. Pat. 149,593) a process of extracting sugar from the beet without the use of diffusion, a process resembling that used by Achard 125 years ago (*see* Note on p. 448). The beet slices (containing 75 to 80 per cent. of water) are pressed, giving a juice of 20° to 25° Brix. The remaining pulp is then heated to 85° with more dilute juice (15° to 17° Brix), which is thus enriched with sugar extracted from the pulp. The latter is compressed in a powerful press in the hot, the residual pulp being rich in sugar and hence of greater value for cattle-food. This process yields less molasses and more *first-jet* sugar, while it requires less expenditure of water, coal, and labour, and a less expensive plant, than when diffusers are used. For each quintal of beet there are 45 litres of water less to evaporate. The Steffen apparatus is shown diagrammatically in Fig. 310. The beets pass into an ordinary slicer, *H*, and the slices fall into *G* and then into a horizontal cylinder, *M*, containing the juice heated to 95° to 98° (600 litres of this juice and 100 kilos of cold slices give a mixture at 85°). A horizontal screw, *Z*, transports the slices to *T*, where they meet a double-jacketed (the inner casing perforated) worm-conveyor, *F*, which raises them and presses them to some extent, so that the juice runs back into *M*. At the top of this conveyor they are discharged into a press of the type described on p. 455 (Figs. 307, 308). The expressed juice returns through the tube, *V*, to *M*, while the pulp falls into *Y* and is conveyed to the drying apparatus. In order to maintain the juice at a temperature of 85°, part of it is continually forced by the pump, *P*, through the tube, X_2, to the sieve, K_2, then to the heater, C_1, and through X_3 to the cylinder, *M* ; if necessary, steam is injected by means of the injector, C_2. In order to dilute the juice in *M* so as to keep it always at 15° to 16° Brix, dilute sugar solution from the washing of the defecation mass in the filter-presses (*see later*) is introduced both directly into the cylinder, *M*, at R_2 and into the inclined conveyor at R_1. The excess of juice flows continuously through the funnel, *A*, to the sieve, K_1, which retains finely divided pulp, and then through the tube, X_1, to the defecation apparatus.

This process admits of the rapid treatment of large masses of material, which is heated to 85° in 2 to 3 minutes and yields 70 to 80 per cent. of juice purer than diffusion juice and about 30 per cent. of pulp (containing 70 per cent. of water and 10 per cent. of sugar), which, after drying, contains 10 per cent. of water, 7·6 per cent. of proteins, 0·4 per cent.

of fat, 10 per cent. of cellulose, 36 per cent. of non-nitrogenous extractive matters, 52 per cent. of sugar, and 4 per cent. of ash; the expense of drying in Germany is about 6·5*d*. per 100 kilos of the dry pulp.

The diminution of 2 to 2·5 per cent. in the yield of commercial sugar is compensated in various ways; the dry pulp is worth about three times as much as diffusion pulp and is sold in Germany at 11*s*. per quintal, in addition to which the diffusion process leads to various small absolute losses.

It must be admitted that, after many trials and much discussion, during recent years, the most competent technical opinion varies with regard to the advantages claimed by the Steffen process. It can, however, be stated that only the most efficient diffusion plant can compete with the Steffen process, which up to the present has been found most advantageous in districts and in seasons in which prices for the dried saccharine pulp are more favourable than those of raw sugar.

In 1910 a dozen factories in Germany alone produced 1,300,000 quintals of sugar by the Steffen process.

In a new process devised by Claassen, all the water from the diffusion of the molasses and that resulting from the pressing of the exhausted pulp are used directly for the extraction of the sliced beets in the diffusors. In this manner all the soluble substances of the beet are returned and utilised, so that an increased yield of sugar is obtained with a diminished consumption of water. This process requires, however, much supervision and care.

The new process devised by Hýroš and Rak employs more perfect machinery than the Steffen process, yet is identical with the latter in many points; but the heating to 85° is carried out in three stages and the final pulp is not dried. This process has been little used, but, according to Herzfeld, could be combined advantageously with the Steffen process.

Other processes, such as those of Bosse, Naudet, Garez, &c., are concerned mainly with the rapid heating of the slices below the slicing machine, pressure or diffusion then being employed.

Juice Measurers. These are special automatic apparatus used to measure the juice extracted at intervals from the diffusors, each such quantity of juice being registered automatically on a strip of paper together with the time elapsing between one discharge and the next. This paper serves to control the working, while it also indicates any stoppages taking place. The underlying principle of such apparatus is the same as that on which alcohol meters (*see* p. 146) are based.

The juice is then discharged through coarse filters to remove vegetable fibres, which are eventually rejected. This dilute juice (10 to 12 per cent. of sugar) has a reddish brown colour and is further subjected to a series of operations, to be described below.

Defecation with Lime. In addition to sugar, the juice extracted from the beet contains proteins, *pectic substances* (colloidal substances of the carbohydrate group), and mineral salts. The pectic matters readily ferment, giving two gummy acids (**Pectic Acid**, $C_{32}H_{41}O_{30}$, and **Pectosinic Acid**, $C_{32}H_{46}O_{31}$), which convert the juice almost into a gelatinous mass and partially invert the sugar.

When the fresh juice is treated with lime, if the latter is not in excess, insoluble calcium pectates separate; whilst if excess of lime is present, the juice is liable to lactic and butyric fermentation of the proteins with development of unpleasant odours. If the lime is added to the hot juice, no fermentation occurs and the whole of the organic impurities are precipitated; but it is not possible to avoid a slight excess of lime, which forms insoluble tricalcium sucrate, so that the mass cannot be filtered immediately. Loss of sugar in this way is obviated by passing carbon dioxide through the turbid liquid, this readily decomposing the sucrate with formation of calcium carbonate and liberation of the sugar. Excess of carbon dioxide must, however, be employed, since otherwise an insoluble double compound of sugar with calcium carbonate is formed.

The operation of saturation with carbon dioxide must be controlled rigorously and continuously in the laboratory, since it is the principal source of loss.

The treatment of the juice with lime is carried out at 85° in suitable vessels provided with stirrers. The lime is added in the quantity previously determined in the laboratory (2·5 to 3·5 per cent.), and may be as powder or in the form of milk of lime, the concentration of the latter being measured by means of automatic floating densimeters. Kowalski and Kosakowski have recently shown that if, as was long ago recommended, the juice is

well agitated during defecation and heating, the total quantity of lime required may be reduced to as little as 1·5 per cent. In France and Germany saturation with carbon dioxide is carried out in two phases, and in Austria in three phases.[1] The lime in the juice is estimated by means of soap solution (Pellet's method) in a way similar to that used to determine the hardness of water (vol. i, p. 215).

In order to avoid the risk of redissolving the calcium carbonate (as bicarbonate), the saturation is first carried on for 20 to 40 minutes at a temperature of nearly 90° until a certain degree of alkalinity remains (0·11 to 0·13 per cent.); the juice is then filtered, heated, saturated again for about 15 minutes until the alkalinity falls to 0·02 to 0·04, and finally filtered a second time. In Austria and Bohemia, however, a little lime (0·5 to 1 per cent. leaving an alkalinity of 0·05 to 0·07) is added before the second saturation in the hot (95°). The juice is then filtered and the third saturation carried out at 100° (10 minutes), the alkalinity being reduced to 0·01 to 0·03. After a fresh filtration, the juice is thoroughly heated for a long time in another boiler, again filtered and despatched to the concentrators. In some factories the third saturation is now made with sulphur dioxide, which has a greater purifying action than carbon dioxide and at the same time decolorises the solution. Liquid sulphur dioxide may be employed, but it is cheaper to produce the gas in furnaces (*see* vol. i, p. 244). In some works continuous saturation is practised, but the Austrian system seems to be the best, even though it leaves 0·06 per cent. of alkalinity.

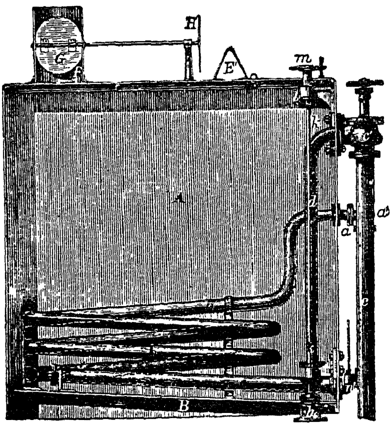


FIG. 311.

The iron saturation vessels (Figs. 311, 312) are provided at the top with a large tube for the escape of the excess of gas. That used for the first saturation is often 7 metres high, but is filled with juice only to the height of 2 metres (30 to 50 hectols.), the remainder of the space gradually being filled with a dense froth; that for the second saturation is 3 metres high, less foam being formed in this case (a large saturation chamber is shown in Fig. 313). If too much froth forms, it can be reduced by the addition of a little coco-nut oil.

The juice is heated for the first saturation by means of a steam-coil, and the carbon dioxide is introduced at the bottom by a perforated tube, *b*. A glass is inserted to permit of the operation being viewed, and a closed orifice, *E*, serves for the inspection and cleaning of the interior.

The completion of saturation is shown by phenolphthalein paper, which ceases to turn violet. Trained workmen also carry out titrations.

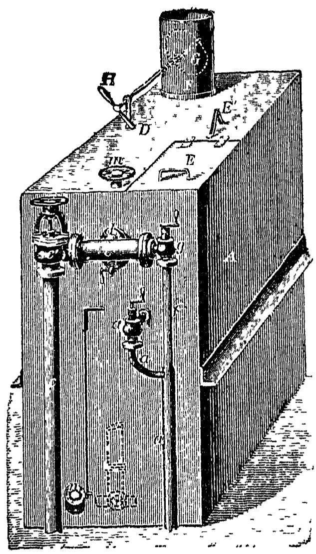


FIG. 312.

A plant for saturation with sulphur dioxide is shown in Fig. 314. The air-pump, *A*, feeds the sulphur furnace, *B*, and the mixture of air and sulphurous acid then passes through the tube, *C*, into the saturator, *D*, the excess issuing by the tubes, *E*.

[1] The lime and carbon dioxide used in sugar-works are generally prepared in a vertical lime-furnace (*see also* vol. i, p. 489), the upper outlet of which communicates with one or two water-cisterns, into which the gas is drawn by an aspirator to be washed and cooled before being conveyed to the saturators. Chalk of good quality (free from iron and containing little sulphate or silica) is used and is mixed with 9 to 10 per cent. of coke (anthracite should be avoided, in order to prevent the presence of odorous and tarry impurities in the gas). The gases contain about 30 per cent. of CO_2, and the size of the suction-pump is calculated on the basis that every quintal of lime produced corresponds with at least 300 cu. metres of gas. The treatment of 5000 quintals of beet per 24 hours requires about 300 quintals of chalk (occupying, in lumps, about 15 cu. metres), which give 170 quintals of quicklime with a consumption of about 85 quintals of coke (9 3 cu metres in lumps).

Continuous saturation processes with a counter-current of juice and carbon dioxide (Horsin-Déon, Raboux) are also used, but they do not seem to have any great advantage.

Behm, Dammeyer, and Schalmeyer propose to purify the juice at 75° with a current of 40 to 50 ampères at 6 to 8 volts for 8 to 10 minutes, using zinc electrodes. This

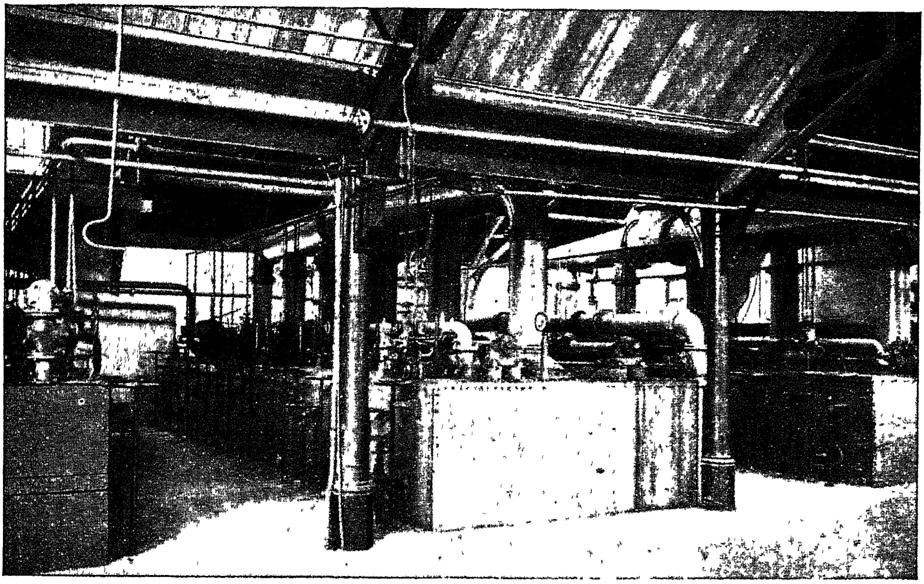


FIG. 313.

treatment seems to result in the deposition of various organic impurities, but, although promising well, the process has not been adopted.

Filtration of the Defecated, Saturated Juice. The precipitated calcium carbonate is separated by passing the juice through *filter-presses*,[1] which allow the clear sugar-juice

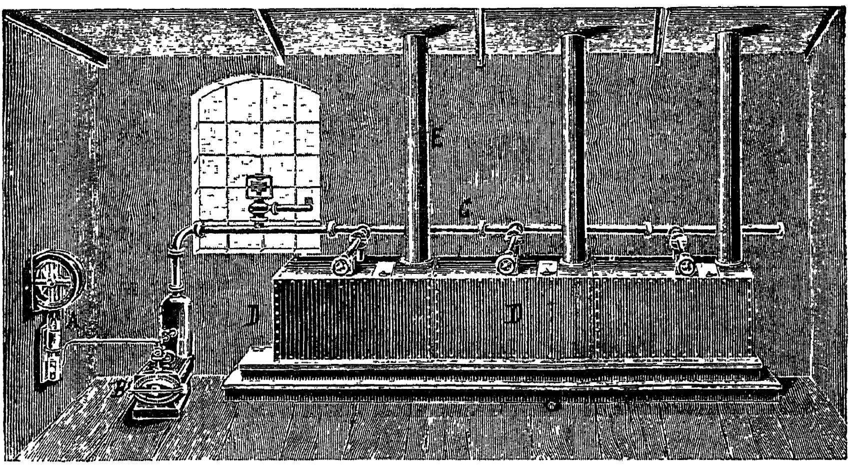


FIG. 314.

to pass through and retain the suspended impurities and the calcium carbonate in the form of cakes, which, after being washed, are readily extracted by unscrewing the press

[1] **Filter-presses** are formed of a number of iron frames, alternately empty and filled in and supported on two horizontal, parallel rods. An empty frame is shown at *A* (Figs. 315, 316) and a filled-in one at *B* (Fig. 317). The latter is filled in with sheet-iron grooved on both sides, the grooves ending below in two horizontal channels

and removing the frames; they fall into conveyors or trucks underneath, and are often used as lime fertilisers. The first wash-water is added to the filtered juice, while the last is used to slake the lime for defecation. The pressed cake should contain less than 0·6 per cent. of sugar.

The filtering surface of the filter-presses necessary after the first saturation is calculated at 0·5 sq. metre per ton of beet worked in 24 hours; after the second saturation

communicating with a single tap, *r* (Fig. 317); the grooves of the two sides are covered with a perforated plate. On the empty frames are stretched cotton or linen cloths, which form two filtering surfaces of the same area as the frame. The frames are squeezed together and against the strengthened block, *P*, by the screw, *V*, so that

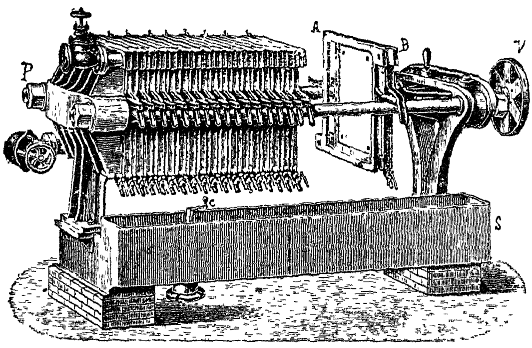


Fig. 315.

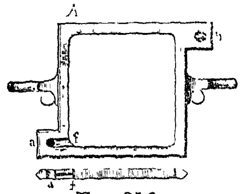


Fig. 316.

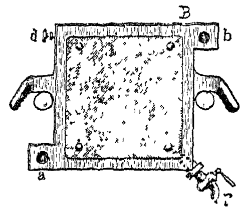


Fig. 317.

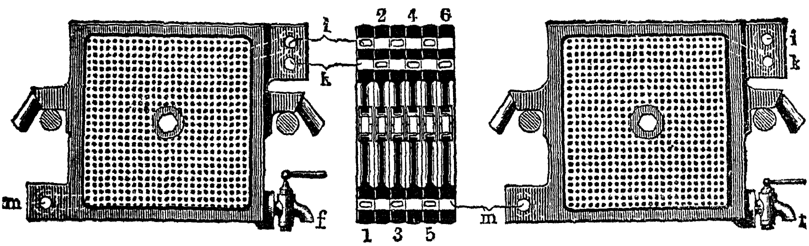


Fig. 318.

hermetic joints are formed at the edges of all the frames. Each frame is provided with bored projections, *a* and *b*, at the top and bottom. When the frames are joined up, the holes in the projections form two continuous channels. The turbid juice enters at *a* and thence passes through *af* into all the empty frames, the air being forced out from these through the valve, *d*. When *d* is closed, the juice passes under pressure through the cloths on the two sides and the clear liquid flows down the grooves and is discharged at *r* into the tank, *S*. When the frames, *A*, are filled with calcium carbonate, the latter is washed with water to remove the sugar it retains. Since only the alternate grooved plates communicate with the tube, *b*, water introduced under pressure at *b* will pass through the cakes of calcium carbonate in the direction of their thickness and into the grooved plates (not communicating with *b*) to be discharged at the taps *r*. In this way, each cake is brought into thorough contact with the washing water, which can be measured in *S*.

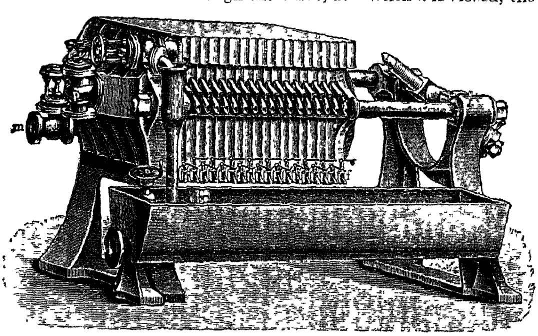


Fig. 319.

In other filter-presses there are no empty plates (Figs 318, 319), but each of these has a central aperture over which the filter-cloth, with a hole exactly in the middle, is screwed with a ring from both sides. The juice is introduced into the chambers between adjacent plates, and the wash-water passes under pressure into alternate (odd) plates from the tube, *m*, traversing the cakes, and collects in the other alternate (even) plates which communicate not with *m* but with *k*, the wash-water being thus discharged; the air is initially discharged from the odd frames through *i*. Each press contains 20 to 50 plates, each 3 to 5 cm. thick, and with a length of side 60 to 100 cm. The juice to be filtered is pumped in under a pressure of 3 to 4 atmos.

0·25 sq. metre suffices. The pressed cakes of chalk form 12 to 14 per cent. of the weight of the beets (*i.e.* four times the weight of quicklime used). The washing of these cakes requires 1 litre of water per kilo.

After the second and third defecations, use is often made, not of filter-presses but of *mechanical filters*, which also serve for removing suspended matter and residues of the slices from the diffusor-juice.

During the whole of its course from the diffusors and saturators, the juice is under pressure and should rise in temperature from 70° to 100°; but since heat is lost in all the pipes, in order that monocalcium sucrate may not be deposited or the liquor become turbid, the use of *heaters* is necessary for the first and second saturation juices, &c.

These heaters consist of a species of tubular boiler divided into three parts by two plates, *p* (Fig. 320); each of the two end parts is divided into 10 chambers communicating in pairs at the two ends alternately. Opposite chambers are connected by groups of long tubes, 4 to 5 cm. in diameter, through which the juice circulates; steam enters at *C*, follows a sinuous path round the partitions, *V*, and finally issues at *D*. The juice enters, at *A*, chamber 1 of compartment I, and passes through the tubes to chamber 1 of compartment II, then to chamber 2 of compartment II, through the tubes to chamber 2 of compartment I, and so on, until it reaches chamber 10 of compartment I and hence leaves the heater at *B*.

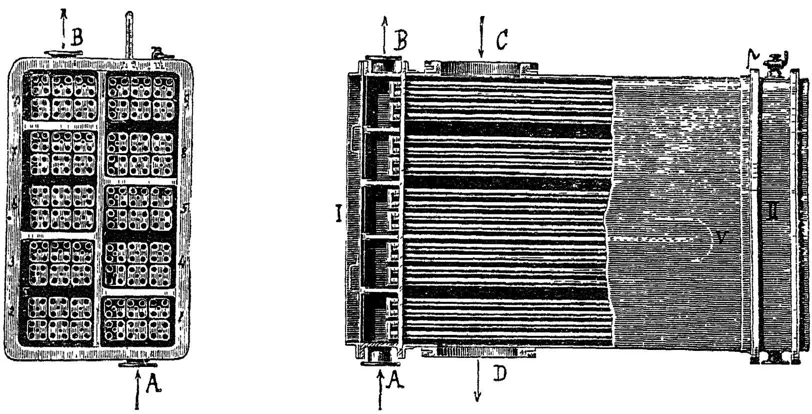


FIG. 320.

After the third saturation the juice passes into a final heater or boiler, where it is thoroughly boiled but not under pressure. The juice is moved by means of pumps, a separate one being used after each operation (for raw juice, first saturation juice, second saturation juice, &c.); double-action piston pumps or Girard pumps, with an efficiency of 80 to 85 per cent., are employed.

When the tax is based on the volume and density of the defecated juice, before the latter goes to the evaporators it passes into tanks under the supervision of the Inland Revenue authorities, who measure the density at 85° to 90° and then reduce it to the normal temperature by means of tables. Thus, in Italy, up to 1903, tax was paid on 2000 grms. (before 1900, only on 1500 grms.) of sugar for every hectolitre of juice and every one-hundredth of a degree of density above 1.

CONCENTRATION OF THE JUICE. The defecated, saturated, and filtered juice is pale yellow and perfectly clear; it contains 88 to 90 per cent. of water, 10 to 11 per cent. of sugar, and 0·8 to 1 per cent. of salts. The formation of crystallised sugar requires first considerable *evaporation* or concentration and then boiling.

The suggestion was made in 1907 to concentrate juice by freezing and removing the ice (E. Monti, Ger. Pat. 194,235), but so far as is known this process has yielded no practical results.

Evaporation is nowadays carried out excusively with indirect steam and in *multiple-effect* vacuum plant. The vacuum is obtained by means of pumps, combined with a barometric water-column, this method being introduced into the sugar industry by Rillieux (*see* modern triple- and sextuple-effect apparatus, vol. i, p. 442 *et seq.*); it admits of

considerable saving in fuel and avoids blackening or caramelisation of the juice, the boiling-point being lowered as the vacuum is increased.[1] The steam from the first body is not all utilised for the second body, part of it, and also part of that from the second body, serving to heat other plant (boilers, heaters, &c.).

The first body is usually heated by the exhaust steam from the engines, which it leaves at a pressure of 1·5 to 2 atmos. The evaporation bodies are simply large wrought or cast iron (formerly copper) boilers surrounded by an insulating earth. These bodies are of various shapes and are placed sometimes vertically and sometimes horizontally. They are usually divided into three compartments by means of two partitions, held rigid by a number of brass tubes, 2 to 2·5 cm. in diameter, connecting the first and third compartments. In boilers with horizontal tubes (Figs. 321, 322, 323) the steam circulates in the tubes in a similar manner to the juice in the heater described above (Fig. 320), while the juice surrounds all the tubes. In vertical bodies (Fig. 324) the steam, entering at *A* and issuing at *B*, circulates in the chamber between the two partitions and heats the numerous connecting tubes. The saccharine solution is thus brought into a condition of vigorous ebullition and circulates rapidly between the lower and upper chambers, as indicated by the arrows in the figure. The level of the liquid, which can always be controlled by the external glass tube, *a*, is kept just above the tubes; in this way, less scum is formed, the free vapour space is increased, and danger of caramelisation is avoided. The boiling may be observed through the window, *r*. In order to separate the drops of liquid carried away in the steam, about two-thirds of the way up the boiler is placed a plate, *P*, with a large central aperture, *C*, above which is arranged a kind of metal umbrella, *p*, at a height adjustable by the levers, *e*, *w*, and *h*. This height is chosen so that the liquid condensing above *P* contains no sugar.

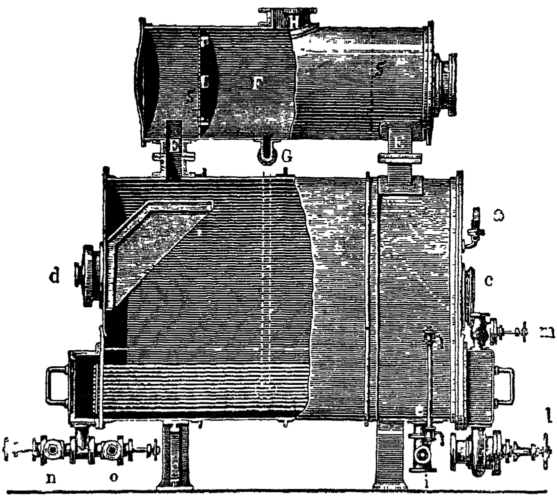


FIG. 321.

But with horizontal evaporators the *spray separators* consist of large cylinders placed above the boiler (*F*, Fig. 321). The steam issuing from the boiler by the tubes, *E*, before passing to the exit pipe, *H*, traverses the finely perforated vertical plates, *S*, which retain the drops of solution carried over by the steam, this effect being facilitated by the expansion and consequent slackening of the steam in *F*. The condensed liquid is returned to the bottom of the boiler by the tube, *G*.

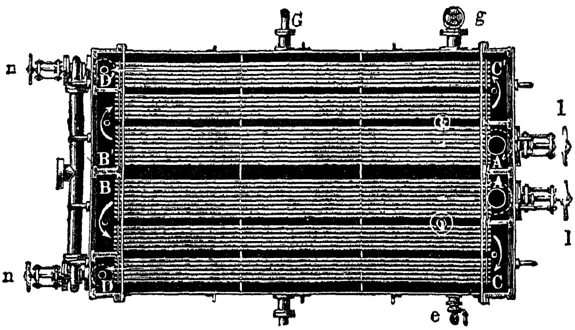


FIG. 322.

[1] The *boiling-point of water* for different degrees of *vacuum* is as follows (Regnault-Claassen): with a vacuum of 50 mm., 98·1°; 100 mm., 96·1°; 150 mm., 94°; 200 mm., 91·7°; 300 mm., 86·5°; 400 mm., 80·4°; 500 mm., 72·5°; 600 mm., 61·6°; 650 mm., 53·6°; 700 mm., 41·7°, 720 mm., 34·2°; 740 mm., 22·4°; 750 mm., 11·8°. It must, however, be remembered that saccharine solutions boil at higher temperatures than water. Thus, under the ordinary pressure, a solution containing 30 per cent. of sugar boils at 100·6°; 60 per cent., 103·1°; 80 per cent., 110·3°; 85 per cent., 115°.

In exceptional cases, where a large amount of spray is persistently formed, this may be diminished by the addition to the boiler of a small quantity of coco-nut oil.

Fig. 325 shows a triple-effect horizontal evaporator of the Wellner-Jelinek type, Fig. 326 a vertical triple effect, and Figs. 327 and 328 a vertical quadruple effect evaporator,

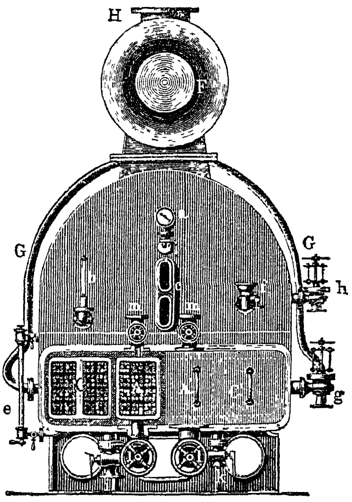


Fig. 323.

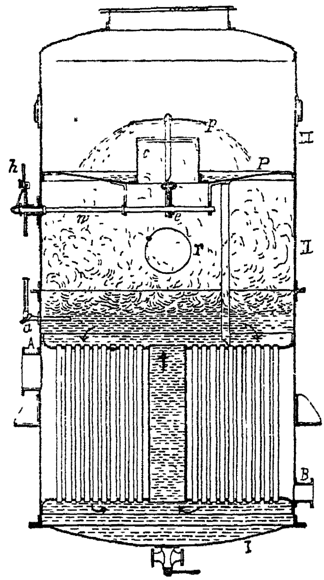


Fig. 324.

in elevation and plan. In the last of these, the steam passes from the body I through the tubes, *a* and *a′*, to heat body II, the steam from which heats body III, and so on ; the steam from the last body, IV, proceeds through the tube, *N*, to the vacuum pump and the barometric water-column.

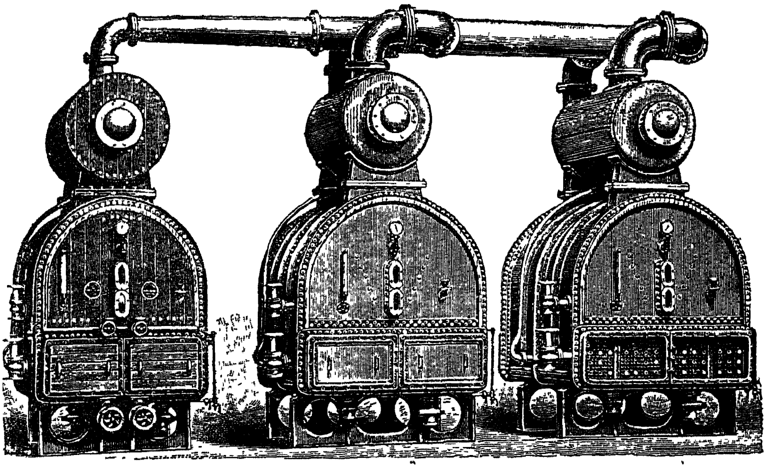


Fig. 325

The evaporation in the separate bodies takes place under reduced pressure in the following manner. In a quadruple effect, steam at a temperature of 110° to 120° (from a boiler or from the exhaust of an engine) enters the tubes of body I, which contains a juice already concentrated to a considerable extent in the other evaporation bodies. Since the steam generated in body I proceeds to the heating tubes of II, where it condenses, a partial vacuum (*e.g.* of 150 mm.) is established in body I, in which boiling will hence take place at a temperature, say 94°, below 100°, and this will be the temperature of the steam which

heats the second body. But the steam given off by the rather more dilute solution of body II is larger in amount, so that a more marked vacuum (up to 350 mm.) is produced by the vigorous condensation of this steam in the heating tubes of body III; the sugar solution of body II will hence boil at about 84°, and steam at this temperature is able to boil the more dilute liquid of body III, where the vacuum may be as high as 380 mm.,

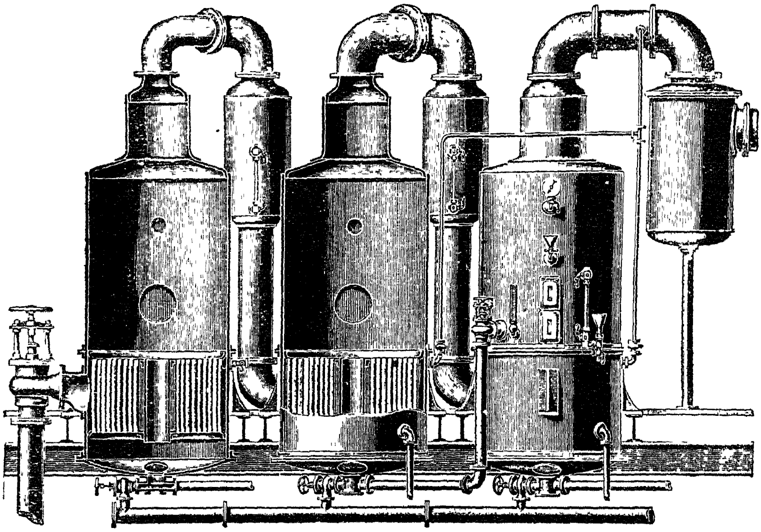


FIG. 326.

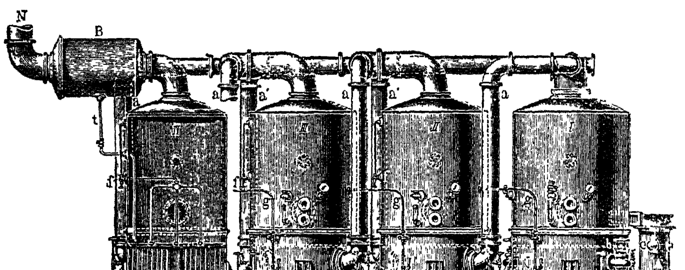


FIG. 327.

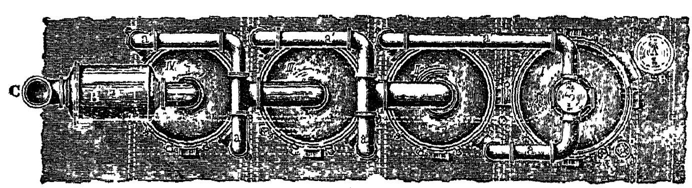


FIG. 328.

corresponding with a boiling-point of 74°. The steam here produced goes to boil the defecated diffusion juice, which is introduced into body IV; the latter is connected with the vacuum pump and with the barometric column, which produce a vacuum of about 630 to 640 mm., corresponding with a boiling-point of about 56°.

When the solution in body I has attained the desired concentration, it is discharged and replaced by that from body II, which in its turn is filled by that from III. The latter

is then charged with fresh juice by means of the tube, *C* (Fig. 329), which also serves for the passage of the juice from one vessel to the other. The steam is circulated between the various bodies by the tubes *G* and *H*, and every battery of heating tubes is connected with a condenser and separator, *l*.

Fig. 329 shows the arrangement of the three barometric columns, *M*, *P*, and *R*, which produce the vacuum directly in the third body of a triple-effect evaporator (for small single- or double-effect plant one barometric column suffices). The pipe, *K*, conveys the steam from body 3 to the chamber, *L*, furnished with an iron barometer tube, *M*, at least 12 metres long, which dips into a well or water-tank, *T*. The condensation water collects in the tube, *M*, to a height corresponding with the vacuum formed in *L*, and hence in the body 3. But the majority of the steam condenses in the chamber, *N*, into the top of which the tube, *O*, introduces a fine cold-water spray which produces an abundant and rapid condensation of steam and a considerable lowering of pressure, so that a large quantity of hot water passes into the vessel, *U*, from the barometer tube, *P*. A little steam condenses in the chamber, *Q*, communicating by the tube, *S*, with the suction pump which maintains the vacuum. The vacuum pump can also be connected, by means of three narrow tubes, with the three evaporation bodies, in which the vacuum can be regulated as desired. It is evident that in the three evaporation bodies, especially in *P*, the water must not be kept at too high a temperature, so that it may not evaporate in its turn and may help the condensation of the steam.

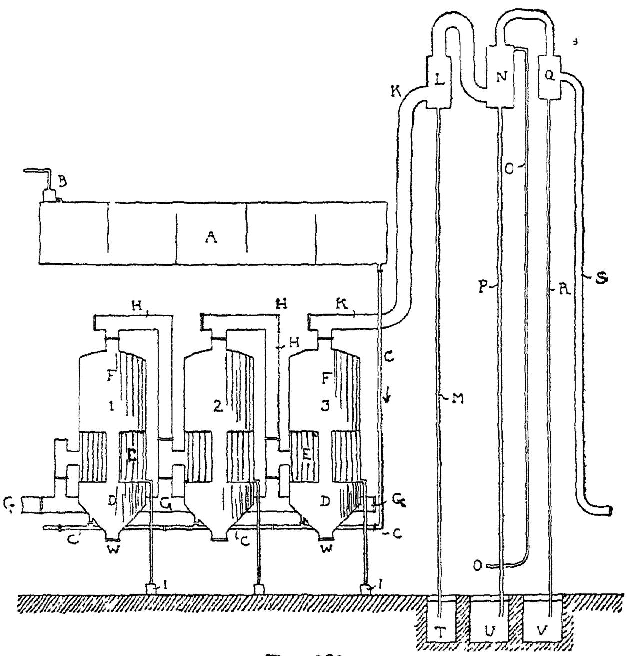


FIG. 329.

Certain sugar-works have recently made successful use of the Kestner concentration system (*see* vol. i, p. 443), which gives an evaporative efficiency superior to that of the ordinary multiple-effect apparatus. Indeed, when there is a difference of, say, 7° between the temperature of the steam in the boiler (*e.g.* 135°) and that of the heated juice (*e.g.* 128°), an evaporation of 80 kilos of water per square metre of heating surface (*i.e.* 11·4 kilos per degree of temperature difference), is obtained with a reduction of the *coal consumption* to 5 kilos per 100 kilos of beet.

In factories where there is not an abundance of water (that required by vacuum plant is ten to twelve times the quantity of juice to be concentrated), it is convenient to utilise the hot condensed water from the steam-engines (an engine of 350 to 400 h.p. requires about 1 cu. metre of water per minute for condensation) and that from the vacuum concentration batteries. This water is cooled in suitable *atmospheric coolers*, *T* (Fig. 330), so that it can be used in the barometric tubes and also for the washing and hydraulic transport of the beets. The tank, *K*, corresponds with that marked *U* in the preceding figure. A pump, *A*, forces this water to the top of the pile, *T* (*see also* vol. i, p. 454), whence it flows down over the faggots built up under a kind of hood, which produces a strong upward draught of air and so evaporates and cools the water (*e.g.* from 50° to 60° down to 25° to 30°). The latter collects underneath in the tank, *r*, and is then transferred by the pump, *M*, to the chamber, *F*, where the dissolved air is separated and passes out through the pipe, *g* (higher than *G*). The water rises in the tube, *G*, to the top of the barometric condenser, *C*,

which is evacuated by the pump, *B*, and the tube, *n*; the pipe, *V* or *S*, corresponds with the tube, *K*, of the preceding figure and communicates with the third evaporation body.

Other more efficient arrangements are also used for the cooling of the hot water. Fig. 331 shows a system consisting of numbers of vertical rods arranged in layers crossing one another in a manner similar to those of the apparatus depicted in Fig. 244 (p. 283). The hot water, entering by the pipe, *A*, is distributed homogeneously by means of the tooth-edged channel, *C*, and collects in the vessel, *B*, underneath; the air drawn upwards between the rods carries with it a cloud of steam. Another arrangement is shown in Fig. 332; here a wooden cap or cover fits over walls composed of sticks arranged in the form of venetian blinds, while at the bottom a Korting injector produces a powerful jet of pulverised water in the shape of an inverted cone. The upward air-current evaporates the water while the latter ascends or while it flows down in a thin film on the boards (in this manner only 4 per cent. of the water is lost). Equally ingenious and simple is the

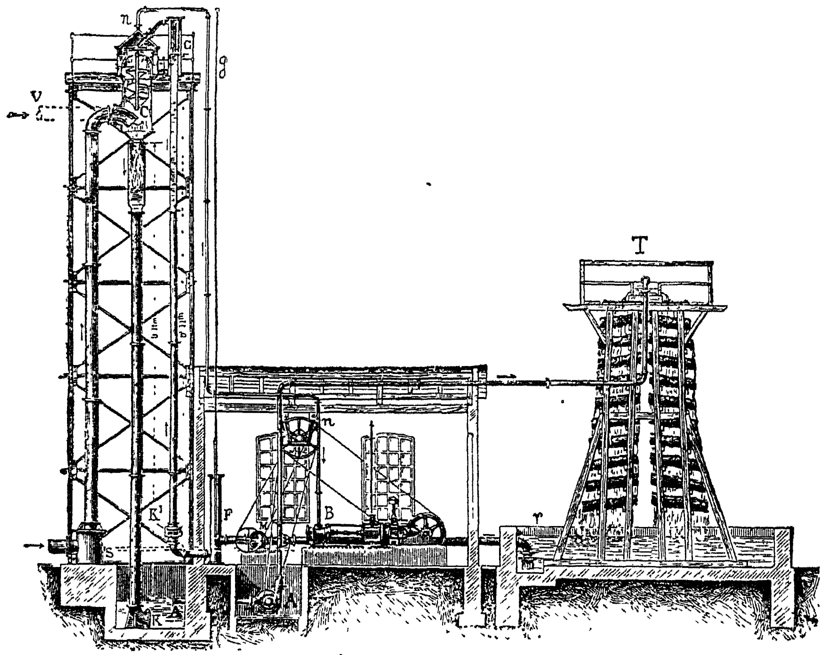


FIG. 330.

cooling effected by forcing the hot water under pressure into a circular pipe fitted with a number of Körting pulverisers, catching the water in a large tank and, if necessary, passing it again through the pulverisers (Fig. 333); but by this procedure more than 10 per cent. of the water is lost.

In those seasons of the year and on those days when the air is warm and dry, the temperature of the water can generally be reduced to that of the air; but if the air is cold and not very dry, the temperature of the water remains 6° to 7° above that of the atmosphere.

BOILING OF THE CONCENTRATED JUICE. The juice from the evaporators has a density of 28° to 30° Bé. (=50° to 55° Brix) and an intense brown colour, and in order to induce crystallisation of the sugar it is necessary to concentrate it until not more than 15 per cent. of water remains (85° Brix). This concentration or *boiling* is carried out in simple vacuum boilers or *vacuum pans*, the juice being first filtered through mechanical filters, collected in tanks and drawn into the pans which are already evacuated.

These pans resemble ordinary evaporators and are made of sheet-iron; they may be either horizontal (like that shown in Figs. 311 and 312) or vertical. In the lower part of the pan is a dense coil of copper or brass pipes arranged either in a zigzag manner or in concentric circles, and through these passes the steam (Fig. 334); in some cases, however, the bottom of the pan is steam-jacketed (Fig. 335). The concentration or boiling is carried

out at as low a temperature as possible and the pan is fitted with a froth-separator (*see* Fig. 311), a tap for the removal of test-samples of the mass towards the end of the operation, and a wide discharge pipe, *K*.

The first thing to be done is to evacuate the pan by connecting it with the condenser and with the vacuum pump. Next the cock of the tube dipping into the concentrated juice tank is opened, the required quantity of juice being allowed to enter. Steam is then passed

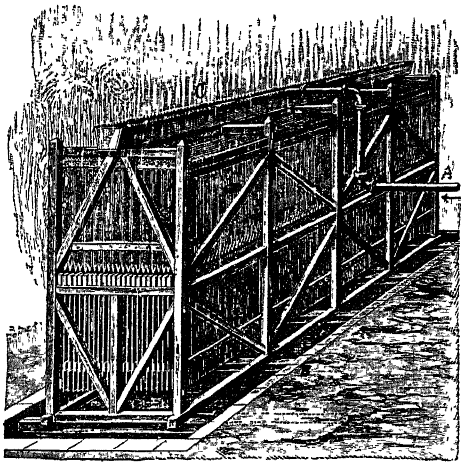


FIG. 331.

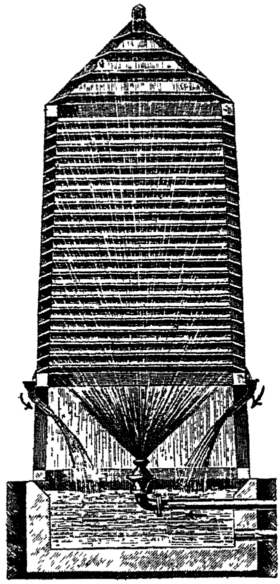


FIG. 332.

through the heating tubes. During the boiling, the level of the juice is not allowed to fall beneath the top of the heating tubes, since otherwise sugar would dry on these tubes and be decomposed ; so that fresh concentrated juice is introduced from time to time. At a certain stage of the concentration small crystals begin to form and gradually increase in size. The operator extracts samples and spreads them out on glass in order to ascertain the size of the crystals and the density of the mass, and when he considers that sufficient of this *massecuite*—consisting mainly of crystals with a certain amount of dark molasses—

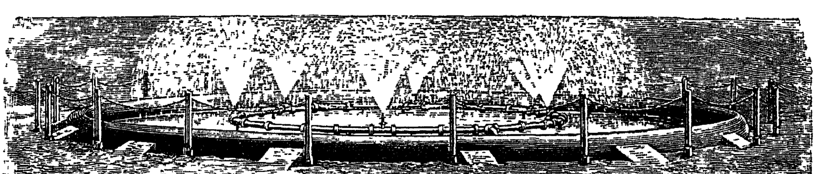


FIG. 333.

has been deposited on the tubes, the heating is stopped and the ordinary pressure established in the pan. The whole mass is then discharged from the outlet, *K*, into a large vessel furnished with stirrers, where it is gradually cooled and the crystallisation completed. The boiling and discharging of the massecuite occupy altogether about 10 hours. Fig. 336 shows a battery of Bock cylindrical crystallisers fitted with stirrers.

Larger crystals are obtained by adding to the crystallising vessels a little unboiled juice, which lowers the sugar-content somewhat and retards the crystallisation. When no further crystallisation takes place, the mass is discharged, by means of a parachute at the bottom of the crystalliser, into the centrifuges, which readily separate the liquid molasses from the solid sugar.

This process of boiling is termed *boiling to grain* to distinguish it from the *boiling to thread*, now used only in refining. In the latter case the boiling is not continued until crystals form, the proper density of the boiled juice being ascertained by squeezing a drop between the finger and thumb and then sharply withdrawing the finger ; if a filament is

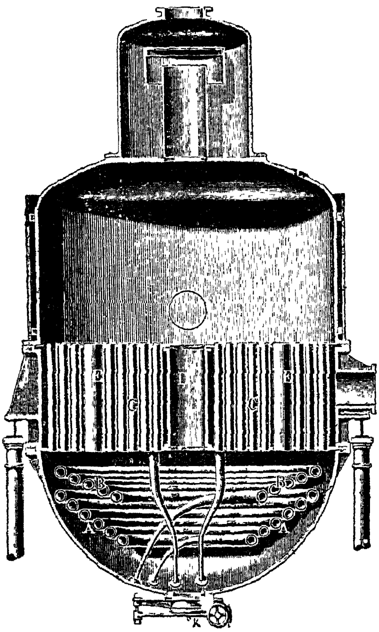


FIG. 334.

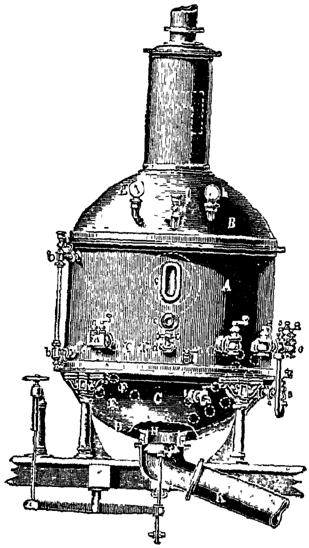


FIG. 335.

thus formed, the boiling is not finished, but the breaking of the thread with formation of two projections indicates the end of the boiling. The syrup is then poured into moulds, which are kept lukewarm until the whole mass sets to an almost solid block composed of finer crystals than in the preceding case.

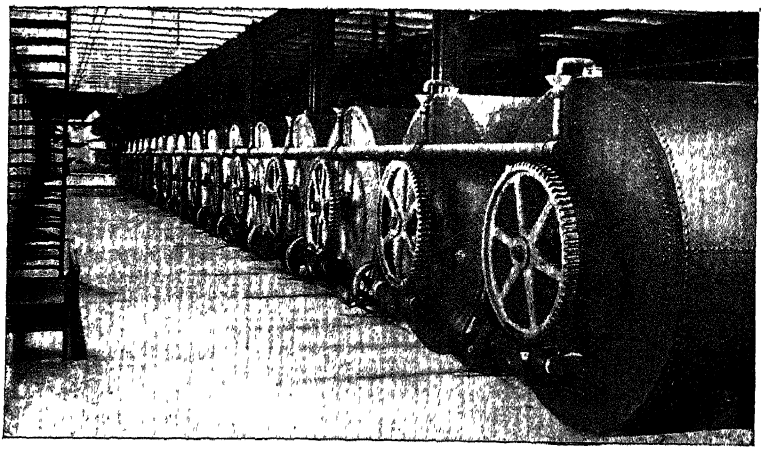


FIG. 336.

CENTRIFUGATION OF THE FIRST MASSECUITE. The centrifuges for the *massecuite* have drums of perforated steel with an inner coating of fine-meshed gauze. The diameter of the drum is about 80 to 100 cm., the height 40 to 45 cm., and the speed of rotation 800 to 1000 per minute. The motive force is applied underneath, and the

centrifuged sugar remaining in the drum is discharged either above (Fig. 337) or through a door which can be opened in the base of the drum (Fig. 338). The massecuite is passed directly from the crystallisers to the centrifuges, and, in order to effect more complete separation of the molasses adhering to the surface of the crystals, especially in the layer adjacent to the gauze, so-called *covering* or *clearing* is resorted to; while the centrifuge is still in motion, the sugar is sprayed with finely divided cold or tepid water (Fig. 339), or even with a jet of steam applied inside or, better, to the outside of the basket, the molasses being thereby rendered more liquid. This procedure naturally gives a whiter raw sugar (first product) but in diminished yield, a small part of the sugar being carried away with the molasses by the water. This loss is diminished by using, in place of water or steam, sugar juices (syrups) gradually increasing in purity, so that the molasses and less pure syrups are removed and the sugar left covered with a solution of pure sugar. In this way minute, moderately white crystals of sugar are obtained, and these are sometimes placed on the market without refining. But the public suspects them of being adulterated and prefers quite white crystals or cubes.

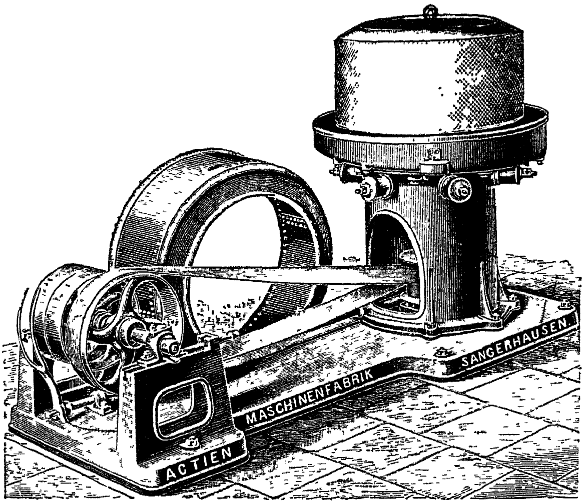


FIG. 337.

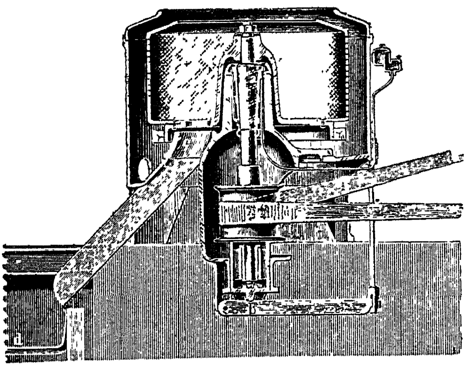


FIG. 338.

The molasses from the centrifugation of the first massecuite, after separation of the *first-product sugar* (first runnings), is further concentrated and boiled in *syrup pans*, which are similar to vertical evaporators and are worked under a vacuum, but are usually of single effect. The boiling is continued until the syrup gives a long thread (*see above*), the impurities present preventing boiling to grain.

This *second massecuite* is then placed in large tanks in the *molasses room*, where it is kept for 25 to 30 days at a temperature of 35° to 40°. The blocks of crystals which separate are broken up with suitable bladed machines, and are then delivered to the centrifuges by means of screws or piston pumps. The resulting *second-product sugar* is rather yellow. The molasses which then separates is further concentrated and the third massecuite sent to the molasses room, but no more sugar separates, since the various potassium and other salts present prevent about five times their own weight of sugar from crystallising. This molasses is hence sold as it is for the preparation of cattle-foods or for the manufacture of spirit (*see* p. 140). In some

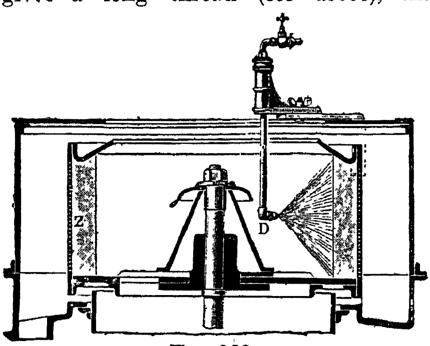


FIG. 339.

countries, however, it is treated by special processes for the extraction of the sugar still present.[1] Every 100 kilos of beet treated yield 1 to 3 kilos of molasses.

The first- and second-product sugars from the centrifuges are sent to the stores, where they are sieved to break up the crusts, which retain molasses. The two products are often mixed, put up in bags holding 100 kilos, and despatched to the refinery.

SUGAR-REFINING. The *raw* sugar (*first* and *second products*, with a purity of 88 to 96 per cent.) is not usually placed on the market, but is purified in refineries, where it is dissolved in hot water, the purer and less coloured qualities of high *rendement*[2] being kept separate from the more impure grades of low rendement.

The solution, with a density of 37° to 39° Bé., is treated with a little lime, with 3 to 4 per cent. of animal charcoal and often with 2 per cent. of ox-blood, after which it is boiled, the frothy crust forming at the surface being continually broken. The suspended matter is then removed by rapid mechanical filters or by filter-presses. The residue (refinery black) is utilised as a manure, while the hot and still coloured solution is passed through a battery of four or six tower filters, 8 to 9 metres in height and 60 to 80 cm. in diameter, filled with animal charcoal (Fig. 340: *A*, tube for dense juice, *B* for dilute juice, *C* for water, *D* for steam) and previously heated with steam (*D*) to prevent the sugar separating and to obtain the maximum decolorising action of the charcoal, this being exerted in the hot.

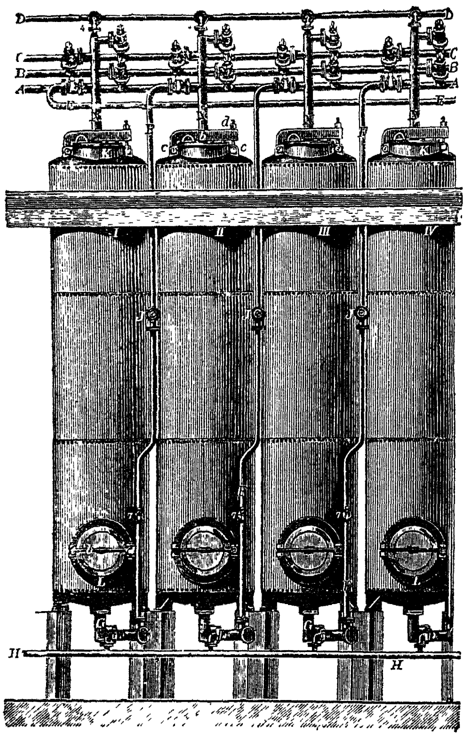


FIG. 340.

The *animal charcoal* or bone-black has a considerable affinity for colouring-matter and for lime, but only a slight one for sugar. But in course of time the pores of the charcoal become obstructed and its decolorising power diminished, so that after a few weeks it becomes necessary to revivify the charcoal.[3]

The solution is passed through the filters in succession and, if necessary, this procedure is repeated. When the syrupy liquid is decolorised, it is concentrated and boiled in ordinary single-effect vacuum pans (of copper) until it shows the grain or short-thread test (*see above*).

When the massecuite reaches this degree of concentration, it is poured into a jacketed copper vessel, in which it is kept at 85° to 90° to initiate the formation of large crystals.

[1] In some works the *second product* is obtained much more rapidly by the Bock or the Grosse process. In the first of these, the molasses is not left for 25 to 30 days in the molasses room but is crystallised in 4 to 5 days by continually shaking in large, jacketed drums heated to 90° to 95° and adding a considerable quantity (25 to 30 per cent.) of crystallised sugar. It is then allowed to cool slowly, but at certain times it is heated one or two degrees above the temperatures it shows at those times, so that the smaller crystals formed, and these only, are redissolved. When the mass has been cooled to 35°, the crystalline blocks are crushed and centrifuged, the amount required (25 to 30 per cent.) to induce the molasses (*see above*) to crystallise being previously removed.

In the Grosse process, the mass is kept in motion by a vertical Archimedean screw rotating in the vacuum pan. With this procedure, crystallisation takes place in 48 hours and, after cooling to 40°, the crystalline mass is disintegrated and centrifuged.

Loblich, Zschene, Stenzel, and others have tried mixing the molasses with fresh juice and defecating the mixture in the ordinary way, but this process does not seem to offer any great advantage.

[2] The *rendement* expresses the percentage of refined sugar obtainable from the raw sugar and is determined indirectly on the assumption that every 1 part of ash diminishes the refined sugar by 5 parts; thus a raw sugar containing 96 per cent. of pure sugar and 0·4 per cent. of ash would give a rendement of $96-(0{\cdot}4\times5)=94$ per cent. The rendement is regarded as low if it is less than 94 per cent.

[3] **Revivification of Animal Charcoal.** The charcoal is first treated with hydrochloric acid to remove the calcium carbonate, and if more than 1·5 per cent. of calcium sulphate then remains, this is eliminated by means of hot soda solution. After washing, the wet charcoal is allowed to ferment (first alcoholic fermentation sets in

It is then allowed to flow into conical copper moulds with their apices, closed by plugs, underneath. The mass, which has just begun to crystallise, is well stirred, and when it has assumed a certain consistency it is left at rest at a temperature of 35°, so that all the molasses collects at the bottom and can be discharged by removing the plug. In order to remove the molasses completely, the sugar-loaves with their casings are introduced into the moulds of a Fesca centrifuge (Fig. 341), which holds sixteen of them, arranged alternately in two superposed series of eight. The point of the sugar-cone communicates with the aperture, *b'*, of the drum of the centrifuge, and when the latter is charged it is fitted in the middle with a cylinder, *h h' k*, which rotates with the drum and is provided with channels, *S*, communicating with all the cones, so that the *covering* solutions (*see above*) may be run in from the tank, *r*. These solutions consist of three or four pale syrups and three or four concentrated solutions of pure sugar. In order to remove the last traces of yellow colour from the sugar and to blue it slightly, as is sometimes required, the final covering syrup is mixed with a minimal amount of ultramarine (5 grms. per 100 quintals of sugar) or methyl or ethyl violet or, better still, according to a recent suggestion, *indanthrene*. The white loaves thus obtained are then dried in suitable chambers or in revolving apparatus, at a temperature of 55°.

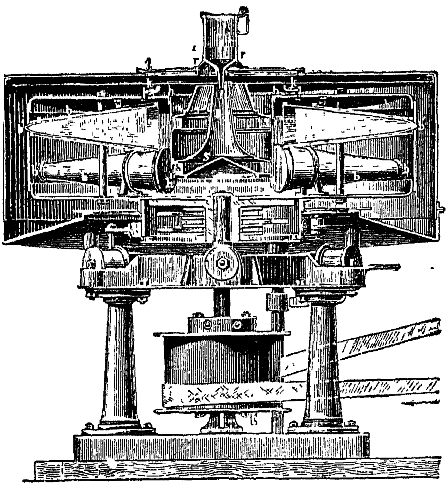


FIG. 341.

To obtain white sugar directly, the final massecuite is sometimes decolorised with 30 to 50 grms. of *blankite* per hectolitre (*see* Note, p. 444 ; blankite is pure, crystallised sodium hydrosulphite, the use of which is rapidly extending in sugar-works ; *see* vol. i, p. 465).

The beet-sugar of commerce should always have a very faint alkaline reaction (towards phenolphthalein), since otherwise it undergoes partial inversion. Cane-sugar, however, has usually a slight acid reaction.

Cube sugar was formerly obtained by sawing the large blocks, this entailing considerable loss. But at the present time suitable centrifuges (Adant type, Figs. 342 and 343) yield directly long rods of sugar of the requisite thickness, these being then sawn with a minimum of loss. A platform, *F*, carries eight vertical prisms, *o*, furnished with screws by which they are fixed to an upper annular disc. The latter is slotted (*c*) to allow of massecuite being introduced into the chambers (*a a*) remaining between each prism and the next, and divided into a number of tall narrow chambers by plates fixed in the grooves, *b*. The platform is introduced into the cylinder, *H*, which fits tightly the periphery of the moulds, these being closed inside by a second cylinder. All the

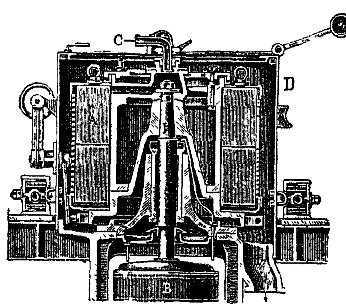


FIG. 342.

then acid fermentation and finally putrefaction), and is afterwards washed thoroughly with water, treated with steam, dried and gently ignited in long cast-iron tubes, *C* (Fig 344), which are heated to about 400° by the gases from the furnace, *A*, access of air to the retorts being excluded. The cooled, free portions are then gradually discharged from the lower parts of the retorts (*E*) into covered metal waggons, so that the charcoal, which is still not quite cold, may not take fire in the air. The discharge of the putrid washing water from the fermented charcoal into rivers causes serious inconvenience, and nowadays this water is either passed on to the soil or subjected to biological purification (*see* vol. i, p. 222).

The plant for decolorising with animal charcoal and the revivifying furnaces are very costly, a large amount of the charcoal at 20*s* to 24*s*. per quintal being required. In 1908, Germany imported 51,666 quintals of animal charcoal and exported 35,019, while in 1900 the imports and exports were 39,839 and 32,018 quintals respectively. Italy imported 4756 quintals in 1908 ; 6789 in 1909 ; and 9863, costing £15,780, in 1910.

Soxhlet avoids the carbon decolorising plant by using filter-presses the chambers of which are filled with a cake composed of wood-meal mixed with various indifferent materials (ground coke or pumice, &c.). By this means sugar solutions can be decolorised moderately well even in the cold.

chambers are filled with massecuite introduced through the slots, *c*, the whole being allowed to cool for 12 to 14 hours with occasional shaking. After complete crystallisation, the whole platform is withdrawn by the crane, *G*, and placed in the centrifuge, *D*,

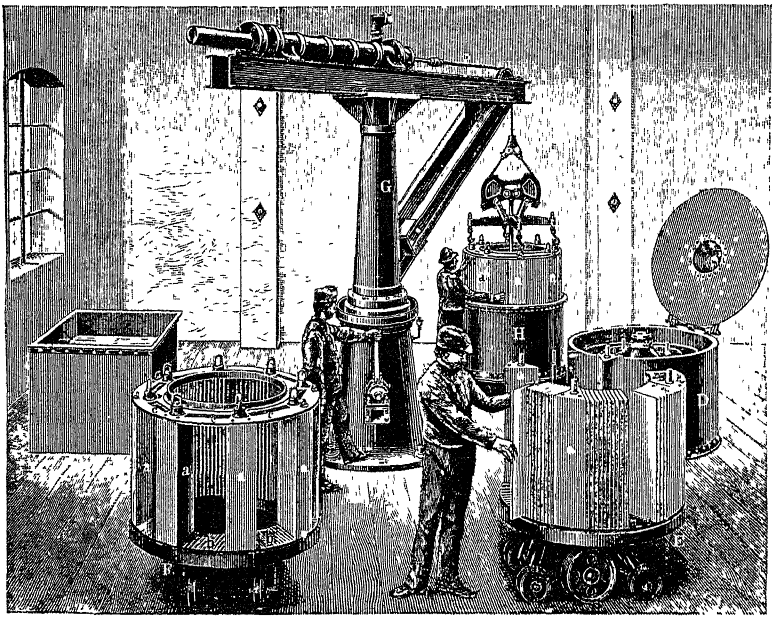


FIG. 343.

which makes about 700 revolutions per minute. The covering is effected at a reduced velocity with sugar solutions entering by the tube, *C*, from a reservoir at a height of 5 metres. After the sticks of sugar have been removed, the platform and moulds are washed with water and are then ready to receive a fresh quantity of massecuite.

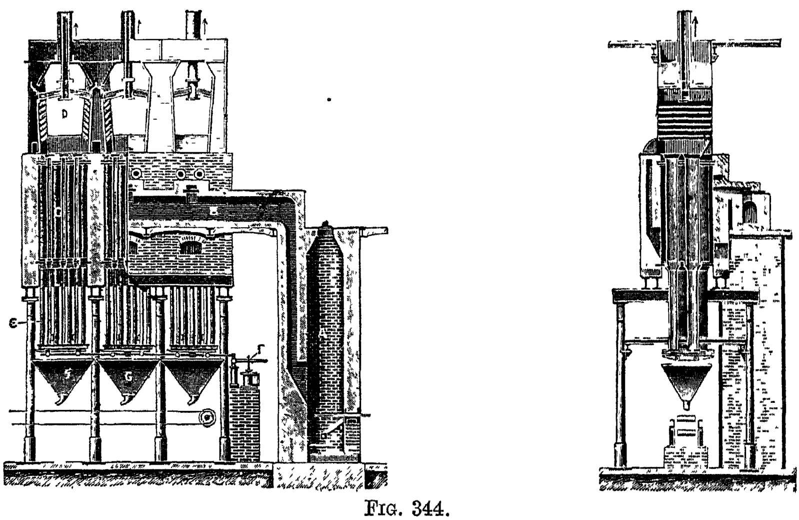


FIG. 344.

Pilé or *crushed sugar* is obtained in a more simple manner by *covering* the crystalline sugar (from massecuite) in the centrifuge itself by means of water, steam, or pure sugar solution. Slight prolongation of the centrifugation yields a hard, compact mass, which is removed in large blocks and broken into small irregular pieces (pilé sugar) by a special crusher having an indented drum (Fig. 345).

Powdered sugar or *farin* is obtained by grinding lump sugar and any scraps between two smooth, horizontal rollers (*d* and *d'*, Fig. 346) which are brought near to one another by springs and are furnished with scrapers, *f*, to detach the powdered sugar ; the latter is subsequently sieved. Powdered sugar can also be obtained by means of the Excelsior mill (*see* Fig. 162, p. 168), which yields as much as 2000 kilos per hour of a sugar not too finely powdered.

UTILISATION OF MOLASSES. The processes employed for the extraction of beet-sugar yield about 3 per cent. (of the weight of beets) of molasses, *i.e.* of dense, dark-coloured syrups, containing 40 to 50 per cent. of sugar. This does not crystallise owing to the presence in the molasses of 8 to 10 per cent. of mineral salts, which prevent about five times their weight of sugar from crystallising. So that, in general, it is difficult or almost impossible to extract sugar by direct crystallisation from syrups with a degree of purity less than 60 to 65 per cent. The percentage composition of molasses varies between the following limits : water, 19 to 28 (mean, 23) ; sugar, 45 to 54 (mean, 48) ; *solids not sugar*, 26 to 29 (mean, 28) ; ash, 6 to 8 (mean, 7 ; largely potassium salts) ; invert sugar, 1·25 to 1·85 (mean, 1·65). The degree of purity ranges from 62 to 67 per cent. (mean, 64 per cent.). The compositions of various Italian molasses have been given in the Note on p. 140.

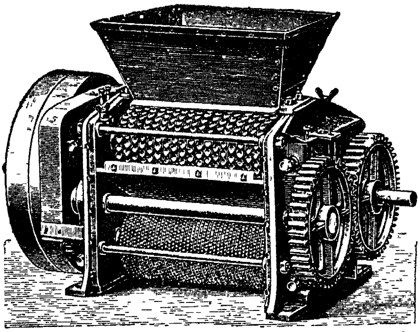


FIG. 345.

The recovery of the sugar from molasses involves indirect processes which are not always convenient in practice, and when this is the case the molasses is employed for the manufacture of cattle-food or spirit (*see* p. 140). In spirit factories the molasses is diluted to 12° to 14° Bé. (about 15 per cent. of sugar), when it can be fermented (*see* p. 140). 100 quintals of molasses yield 23 to 25 hectols. of alcohol (calculated as anhydrous spirit) and 1800 kilos of CO_2. The potassium salts are extracted from the residual vinasse by the process described in vol. i, p. 435. 100 kilos of molasses give 35 kilos of concentrated vinasse (40° Bé.), and by calcining this 10 kilos of *vinasse charcoal* are obtained. In some factories the vinasse is now treated for the recovery of the ammonia and fatty acids by the Effront process described on p. 155, without, however, losing the potassium salts.[1]

In Italy, before the modification of the fiscal regulations which taxed the defecated saccharine

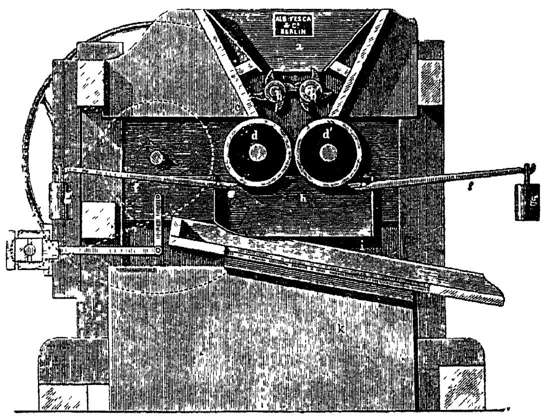


FIG. 346.

[1] The *molasses vinasse* remaining after the distillation of the alcohol has a density of about 4° Bé. and contains 6 to 7 per cent. of solids. When utilised, it is first concentrated to 40° Bé (100 kilos of molasses give 35 kilos of this concentrated vinasse), when it contains 75 per cent. of solids with about 4 per cent. of nitrogen. About one-half of the solid substances are nitrogenous compounds. The solids contain 10 to 12 per cent. of betaine, 5 to 7 per cent. of glutamic acid, and 1 to 2 per cent. of leucine and isoleucine, besides varying quantities of amino-acids and nuclein bases ; the non-nitrogenous constituents consist of about 15 per cent. of fatty acids (formic, acetic, lactic, butyric, and homologous acids), and 15 to 20 per cent. of other organic compounds not completely investigated. Effront thinks it possible, from 100 quintals of molasses, to obtain 75 kilos of ammonium sulphate and 95 to 120 kilos of fatty acids, by the action of yeasts which decompose the amino-acids into ammonia and fatty acids, separable by distillation. But, according to F. Ehrlich, yeasts transform amino-acids into alcohol and succinic acid, the formation of ammonia and fatty acids being due not to yeasts but to butyric and other bacteria which always occur with yeasts, and decompose the amino-acids into ammonia, fatty acids, and various amines just as in ordinary putrefaction. Hence the effect of the Effront process could also be obtained by adding to the aqueous vinasse a little putrefied meat and allowing putrefaction to proceed. The manipulation of large masses of putrefied liquid would not, however, be very agreeable or hygienic.

juices directly and left untaxed the sugar in the molasses, various factories applied certain of the chemical and physical methods used in other countries for the extraction of the sugar from molasses—by means of osmosis, lime, strontia, baryta (formerly by means of alcohol), &c. When these methods (*see later*) are used, it is calculated that the final molasses does not exceed 0·5 to 1 per cent. of the weight of the original beets.

In Italy the amount of molasses produced annually, including that from refineries, is 300,000 to 350,000 quintals, which is utilised almost entirely in spirit factories, 60 kilos of anhydrous alcohol being obtained from 100 kilos of sugar. Germany produces about 4,000,000 quintals, 2,200,000 being desaccharified by means of strontium, 1,250,000 used as fodder, and 350,000 utilised by spirit factories. In 1908 England imported 84,128 tons for making spirit and cattle-food. In France, 346,000 quintals of molasses were returned to the agriculturist in 1907.

(1) **Osmosis Process.** This was first proposed by Dubrunfaut in 1863, and is based on the osmotic properties of crystalloids, which pass through a membrane immersed in water (*see* vol. i, p. 102). But different crystalloids traverse the membrane at varying speeds, the sugar, for instance, far more slowly than salts. Hence, if the molasses is placed in a dialyser and surrounded with water, after a time the water will contain more salts than

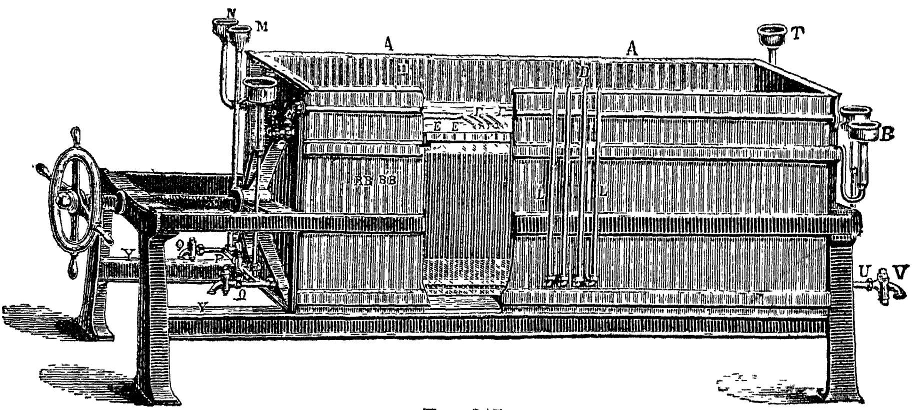


FIG. 347.

sugar, while the molasses will be diluted with water but will contain relatively more sugar and less salts than at first.

The apparatus now used for osmosis (Fig. 347) consists of a series of wooden frames 4 cm. in thickness and of the size of those used in filter-presses ; these are separated by sheets of parchment paper, the whole being pressed tightly together. The compartments thus formed are filled alternately with water and molasses. The upper part of the whole of the osmogen constitutes an open reservoir formed by the upper vertical projections of the frames. The molasses for feeding the alternate chambers is placed in this reservoir and is kept circulating in various ways. The water chambers are fed from the lower part and are discharged through a common upper tube as they become enriched with salts.

The osmotic effects occur best in the hot, so that the molasses is introduced at 80° and the water at 90°.

The taps through which the liquids enter and leave the osmogen are regulated by automatic floats, which close or open the taps more or less so as to maintain a constant relation between the density of the exosmosed aqueous solution and that of the osmosed molasses. This relation is determined beforehand in the laboratory, and corresponds with the conditions least favourable to the loss of sugar with the osmosis water and most favourable to the purity of the residual molasses.

The exosmosed water generally has a density of 3° Brix (3 per cent. of sugar and salt together), and the osmosed molasses 35° to 40° Brix (measured at 75° C.) ; the latter is concentrated and boiled in ordinary syrup pans until it shows the string test. Crystallisation is carried out in the molasses room at 40° to 45° or in the Grosse apparatus. The crystallised sugar is separated by centrifugation and the new molasses obtained again subjected to osmosis. This operation is repeated once or twice more—in fact, until the

quantity of sugar extracted would be insufficient to pay the cost. In some cases the osmosis waters are concentrated and reosmosed.

The final molasses and the final osmosis waters—rich in salts and also in sugar—serve for making spirit, shoe-polish, or potassium salts (*see* p. 155). They are also given to cattle, but must then be diluted with solid vegetable products as an excess of salts may exert harmful effects.

(2) **Lime Process.** Steffen found that the addition of finely powdered, sieved quicklime in small portions to a solution of molasses of a suitable concentration (about 12° Brix, *i.e.* 7 per cent. of sugar, obtained from 1 quintal of molasses + 7 hectols. of water), and kept at a temperature below 15°, results in the separation of insoluble sucrate containing rather more lime than tricalcium sucrate, whilst the impurities remain dissolved in the aqueous molasses.

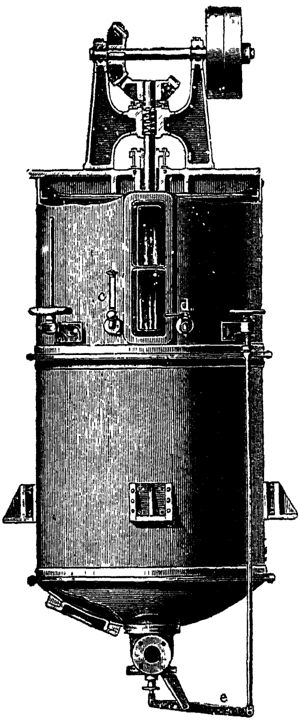


FIG. 348.

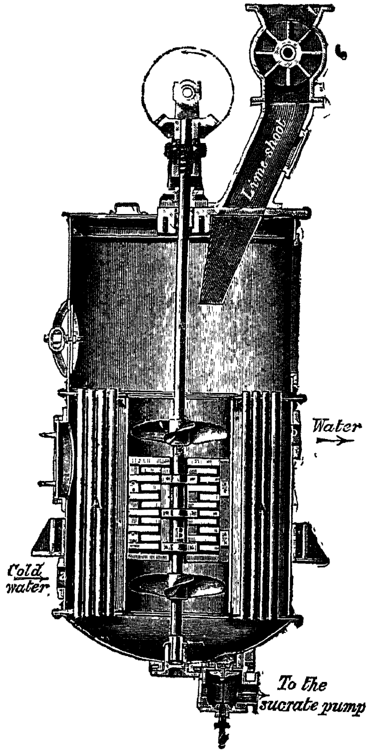


FIG. 349.

The operation is carried out in a vessel (Figs. 348, 349) similar to the Grosse apparatus, the steam-pipes being used, however, for the circulation of cold water at about 12°, so that after each addition of lime, when the temperature rises 7° to 8°, it can be brought rapidly down below 15°. The addition of lime is continued until all the sugar is precipitated (about 100 kilos of lime per 100 kilos of sugar), this being ascertained by reading the clear liquid in the saccharometer.

The resultant sludgy mass is filter-pressed at a pressure not exceeding $1\frac{1}{2}$ atmosphere, the filtrate still containing about 0·5 per cent. of sugar, which can be separated as tricalcium sucrate by heating the liquid to 90° and filtering.

The cakes of sucrate are washed several times in the filter-press and the fairly pure residue used to defecate fresh diffusion juice before saturation with carbon dioxide ; or the sucrate can be treated with any cold saccharine solution so as to form the soluble monosucrate, the precipitated excess of lime being removed by filtration and the filtrate then saturated with carbon dioxide in the ordinary manner.

(3) **Strontia Process.** When an excess of crystallised strontium hydroxide is added to a dilute sugar solution at a temperature of about 100° and the liquid boiled, a granular,

sandy precipitate of strontium disucrate is obtained, which is stable in the hot whilst in the cold it decomposes into sugar and strontium hydroxide.

In a suitable boiler provided with steam-coils and stirrers, a 10 per cent. solution of strontium hydroxide is boiled, further quantities of the hydroxide being added until a 20 to 25 per cent. solution is obtained. The molasses is now added in amount equal to about one-third of that of the strontium solution, which is stirred rapidly and heated meanwhile. Strontium hydroxide is subsequently introduced in such amount that the mass has 12 to 13 per cent. of excess alkalinity. The total strontium hydroxide is related to the sugar in the molasses in about the proportion 2·5 : 1.

The precipitated disucrate is filtered rapidly in the hot through bag-filters and washed with boiling 10 per cent. strontium hydroxide, the latter being recovered from the filtrate. The disucrate is then dissolved in a cold strontium hydroxide solution and the solution introduced into metallic vessels situate in an apartment kept below 10°. In the course of three days one-half of the hydrate separates in a crystalline form, the saccharine solution being then decanted and the residue centrifuged. The sugar solution is then saturated with carbon dioxide until it shows an alkalinity of 0·05, all the strontium being thus separated as carbonate. The very pure sugar solution obtained after filtration is concentrated and boiled as usual, the crystallised sugar obtained being placed directly on the market without being refined.

A somewhat different mode of procedure is that based on the formation of strontium monosucrate, but this does not yield the whole of the sugar as the above process does. In Germany the desaccharification of molasses is effected almost exclusively with strontia in large works specialising in such work.

(4) **Baryta Process.** When solutions of molasses and of barium hydroxide are mixed in the hot in the proportion of 1 mol. of sugar to 1 mol. of the hydroxide, a heavy, sandy precipitate of barium monosucrate is formed which is stable to either hot or cold water; this is collected as usual on filters and freed from impurities by washing with cold water. It is then saturated with carbon dioxide in order to liberate the sugar and, after dilution with other sugar juices, is filtered, concentrated, and crystallised.[1]

YIELD AND COST OF PRODUCTION. Formerly a hectare of land yielded with difficulty 200 quintals of beet, but as the result of long-continued improvement of the methods of cultivation, manuring, selection of seed, &c., as much as 300 to 400 quintals are now obtained, and in certain special regions (*e.g.* Ferrarese) as much as 600 to 650.

Italy contains 20,000,000 hectares of cultivated land (excluding forests), 5,000,000 being under corn, 1,600,000 under maize, and only 50,000 under beet, the yields being as follows:

	Hectares under beet	Mean production per hectare	Mean price per quintal	Mean quantity of sugar per 100 kilos of beet
		Quintals	Shillings	Kilos
1905–1906	37,500	253	2·01	12·24
1906–1907	37,954	271	2·02	13·56
1907–1908	41,000	307	2·15	13·98
1908–1909	51,000	280	—	13
1909–1910	36,000	—	—	—
1910–1911	50,000	—	—	—

For every quintal of beet worked, the loss is calculated to be 1·6 kilo of sugar in Italy

[1] The barium carbonate filtered off is converted into the oxide and then into the hydroxide by heating in suitable high-temperature furnaces (*see* vol. i, p. 502).

This barium process was used for some time in Italy, after it had been shown that no danger to health was to be feared from the use of a barium compound, since this is eliminated completely by carbon dioxide and the final traces by calcium sulphate. The barium hydroxide required is imported principally from America and Germany; but by 1903, four factories had been erected in Italy for supplying all the baryta necessary to the sugar factories. One of these factories, at Calolzio, starts from barium sulphate; another, at Milan, heats the barium carbonate from the sugar-works; while the remaining two, at Foligno and Pont St. Martin respectively, treat barium carbonate in electric furnaces, making first barium carbide, which with water gives acetylene and barium hydroxide (Garelli's process).

Such treatment of molasses in Italy was found feasible as long as the sugar extracted in this way remained free from taxation, that is, while the tax was levied solely on the defecated diffusion juice. But since 1904, the total quantity of sugar produced, including that extracted from molasses, has been liable to duty, and the molasses is consequently utilised in the distillery and in the manufacture of cattle-food. But recently some sugar factories have resorted to treatment of the molasses with barium sulphide, which is much cheaper than the hydroxide and is obtained directly from the sulphate in the electric furnace.

and only 1 kilo in Germany. The cost of cultivating 1 hectare of beet, including manure, transport, &c., amounts to £12.

Italian manufacturers calculate that in bad seasons the production of 100 kilos of refined sugar requires 10 quintals of beet, the cost of working these being 7*s*. to 8*s*. (including 3*s*. for coal). Refining costs about 5*s*. 6*d*. (100 kilos of raw sugar give about 90 of refined).

In Germany 100 kilos of beet gave not more than 8·4 of sugar in 1870, about 12·5 in 1890, and 15·8 (including that from the molasses) in 1909–1910. The mean production per hectare was 246 quintals of beet in 1871 and 300 in 1910.

The consumption of coal in working 100 kilos of beet in Germany was 35 kilos in 1867, 24 kilos in 1877, 10 kilos in 1890, and 7 kilos (8 in Italy) in 1900. By the use of Kestner concentrators (*see above*) a further saving in coal has recently been effected.

Every 100 kilos of beet treated yield 3 kilos of molasses (including 0·5 kilo from the refining process) containing 45 to 50 per cent. of sugar.

Each quintal of beet gives 80 kilos of exhausted and pressed pulp or slices containing 70 per cent. of water.

The cost of manufacturing 100 kilos of *cane-sugar* in Java varies from 12*s*. to 16*s*., and transport to England or the United States amounts to 2*s*. per quintal.

STATISTICS.[1] The history of the development of the sugar industry in Europe and the importance this industry has assumed during the past quarter of a century have already been discussed on p. 448. Reference has also been made to the production of cane-sugar compared with that of beet-sugar. While in 1854 beet-sugar formed only 14 per cent. of the world's total production (1,423,000 tons), in 1866 the proportion was 30 per cent. (on

[1] The Commercial, Customs, and Fiscal Conditions of the sugar industry in Italy and other countries. In some countries this great industry has been extended artificially owing to the direct and indirect help afforded by the State, and to the speculations of financiers. With the excuse of protecting national industries, Governments have levied heavy Customs duties, with the result that the public has paid dearly for its sugar, while manufacturers have accumulated enormous profits and have been enabled to export sugar at less than cost price to other countries. At first the protective duty was from 24*s*. to 32*s*. per quintal, while in France it was raised to 64*s*. The form taken by the protection was then changed by the institution of export bounties, which allowed the sugar to be sold abroad at a low price, while large profits were made owing to the high prices at home and to the bounties. First Belgium and then France established a bounty of 8*s*. to 10*s*. for every quintal of sugar exported, France being thus subjected to an enormous burden amounting to over £2,000,000, without counting the rebate on the freight from the factory to the frontier. This enormous sum has been paid by the mass of the population, to the exclusive advantage of a few manufacturers (rule of the Méline Ministry)

In Germany and Austria, where the export bounties were relatively low, the manufacturers formed sale syndicates (cartels), which operated in the following manner: the manufacturers pledged themselves to supply all the raw sugar to the refiners, who granted a bounty of 24*s*. per quintal to the manufacturer and sold the sugar to the home consumer at a very high price, there being no fear of competition, as they enjoyed a monopoly. The sufferers, as always, were the consumers. The home profits were so enormous that sugar could be sold abroad at less than cost price and competition thus vanquished. On the other hand, England, the greatest consumer of sugar, found its markets deluged with cheap Continental sugar, which competed seriously with that from its Colonies, which had also become considerable exporters.

Under these conditions a more rational solution was found for the problem of sugar with reference to international commerce. The initiation of such an undertaking could come only from England, who was able finally to impose her conditions on all countries sending sugar to her markets. The Brussels Convention, convoked on September 1, 1902, was subscribed to by England, Germany, Austria, France, Belgium, Holland, and Italy. The result was the abolition of export premiums and the reduction of the boundary duty to 5*s*. per quintal above the manufacturing tax, from September 1, 1903, onwards. Such duty was to be enjoyed only by those countries conforming to the Brussels Convention.

Italy did thus conform in a modified way: the boundary duty remained as before, namely, 23*s*. for first quality and 16*s*. 6*d*. for second quality, while a pledge was given not to export sugar to other countries and to impose an exceptionally heavy Customs duty on countries not adhering to the Brussels Convention (especially on Russia and the Argentine Republic; but Russia entered the Convention in January 1908, and pledged herself to export for six years not more than 200,000 tons per annum of bounty-fed sugar. After 1908 England held herself free to import premiumed sugar without imposing supertaxation). Spain and Sweden were treated like Italy by the Brussels Convention, to which then Luxemburg, Peru, and Switzerland conformed. In Spain there is now an overproduction crisis.

This is the regime now in force in Europe. But in Italy the price of sugar fell, owing to overproduction and frenzied competition, to 92*s*. per quintal, so that in 1901–1903 almost all the sugar factories showed either minimal profits or considerable losses. Indeed, deducting the tax of 56*s*, there remains 36*s*. as the price of the sugar. And, according to the manufacturers, 10 quintals of beet, giving 1 of sugar, cost 16*s*, while the cost of production of crude sugar is 8*s*. (including 4*s*. for coal), that of refining about 6*s*. 4*d*. and that of transport 1*s*. 8*d*: total, 32*s*. Thus only 4*s*. remains to provide interest on capital as well as depreciation. Hence, in 1904, all the sugar-makers combined to form a syndicate and raise prices, and early in 1905 an increase of 16*s*. (to 108*s*.) per quintal was enforced; with a production of 1,000,000 quintals, this amounted to an annual burden on the consumer of £800,000. Adding to this the protective duty of £1,200,000, it will be seen that, for the luxury of a native sugar industry, the Italians pay an annual tax of £1,200,000 to £2,000,000, the sole gainers being some 30 factories with a capital of about £3,200,000; this in spite of the fact that Germany and Austria would supply sugar at 24*s*. to 26*s*. per quintal, so that, leaving aside the taxation of £2,800,000, sugar could be sold at 10*d*. instead of 15*d*. per kilo.

The sugar manufacturers state that, owing to various causes, their capital yields on an average only 6 per cent. But it can only be regarded as a mistake to keep an industry alive under such artificial conditions, when the consumer evidently suffers considerable injury and the advantage to the agriculturist and the operative is doubtful and in any case minimal.

Attempts recently made to remedy this state of affairs have been unsuccessful.

a total of 2,000,000 tons); in 1878, 44 per cent. (on 3,000,000 tons); in 1887, 47 per cent. (on more than 5,000,000 tons); in 1893, 55 per cent. (on about 6,000,000 tons); in 1899, 64 per cent. (on 7,500,000 tons); in 1901, 67 per cent. on almost 9,000,000 tons. In 1909–1910 cane-sugar again assumed first place, constituting 53·5 per cent. of the total world's production of nearly 15,000,000 tons. In Europe the total area under beet is about 2,000,000 hectares, about 43,000 hectares being in Italy.

Country and year	No of factories	Production of beets (*b*) or sugar-cane (*c*)	Output of raw sugar	Remarks
Europe		Tons	Tons	
Germany . . 1903	384	12,171,000 *b*	2,293,000	In 1907, 417 factories and refineries worked 14,187,000 tons of beet, obtaining 1,950,000 tons of raw sugar In 1905–1906 the production was 2,400,000 tons, and in 1909–1910, 2,037,400 tons
Austria-Hungary 1903	215	7,542 600 *b* 8,507,000 in 1908	1,290,000	355,000 tons in 1886; 665,000 in 1894; 865,000 in 1900; 1,334,000 in 1906; 1,259,000 tons in 1909–1910
France . . 1903	296	6,315,300 *b*	1,080,000 807,500 in 1909	Equal to 694,000 tons of refined, in 1904, 540,000 tons
Russia . . 1903	275	7,604,000 *b* 8,800,000 in 1908	1,000,000	425,000 in 1887; 578,500 in 1894, 1,300,000 in 1906; 1,144,000 tons in 1909–1910
Belgium . . 1903	100	1,615,000 *b*	325,000	241,000 in 1909–1910
Holland . . 1903	29	1,023,000 *b*	204,000	175,000 in 1909–1910
Italy . . 1909	31	1,050,000 *b*	165,000	Or 150,000 refined
Spain . . 1904	32	580,000 *b*	64,300	69,000 in 1905; 108,340 (in 49 factories) in 1908; 86,000 in 1910
,, . . 1904	27	250,000 *c*	24,500	After 1906 there was overproduction. Cultivated between Gibraltar and Almeria: 28,820 tons in 1905; 140,600 in 1908, 22,000 in 1910
Denmark . . 1903	7	415,000 *b*	65,000	58,500 in 1909
Roumania . 1904	5	182,700 *b*	23,500	
Sweden . . 1909	21	864,400 *b*	122,000	Only 4000 in 1886
America				
United States . 1903	70	1,500,000 *b*	300,000	12,000 in 1893; 327,000 in 1904; 433,000 in 1907; 450,000 in 1909–1910
,, ,, ,,		*c*	170,000	
,, ,, ,,		maple	12,000	5400 in 1880; 10,000 in 1907
Cuba . . 1904		*c*	1,050,600	1,140,000 (home consumption, 26,000) in 1905–1906; 1,450,000 in 1907; 970,000 in 1907–1908, 1,520,000 in 1908–1909; 1,459,000 in 1910–1911
Trinidad . . 1906		*c*	54,000	45,600 in 1907; 41,600 in 1908
Other Antilles, Central America . 1906		*c*	410,000	
South America (Demerara, Peru, Argentine, Brazil) . 1902		*c*	440,000	Argentine in 1909 produced 115,000 and consumed 150,000 tons
Mexico . . 1909		*c*	160,000	143,000 (and 70,000 molasses) in 1908; exports £400,000 to £600,000
Asia				
Java . 1909		*c*	1,312,466	1,285,000 in 1907
Philippines . 1909		*c*	94,000 exported	Production, 122,000 tons in 1907 and 138,000 in 1908
East Indies . 1904		*c*	1,300,000	
Australia . 1902			470,000	
Africa . 1902 (Egypt, Réunion, and Mauritius) . .		*c*	280,000	
Formosa (for Japan) 1910	17	*c*	45,000 (1904) 71,000 (1906) 206,000 (1910)	

The world's *production* of sugar and that of the various countries is shown in the Table on the opposite page, which also gives the number of sugar factories.

The total world's production of sugar is given by about 1400 factories and 300 refineries, and in 1904–1905 amounted to 11,684,000 tons of raw sugar, in 1905–1906 to 13,762,000 tons, in 1906–1907 to 14,420,000, in 1907–1908 to about 13,500,000, and in 1909–1910 to 16,200,000 tons, nine million tons of this being cane-sugar.

In Japan a single refinery at Moji produces 2500 quintals of refined cane-sugar daily, and it is proposed to double the output. Two other refineries are found at Osaka and Tokyo respectively. These work mostly raw sugar from Java and export a considerable quantity of refined sugar to China and Corea. Formosa produced in 1907 about 70,000, in 1908 about 100,000, and in 1910 more than 200,000 tons of cane-sugar.

In 1910 the areas under beet in the various countries of Europe were as follow (hectares): Russia, 675,000; Germany, 470,000; Austria-Hungary, 365,000; France, 235,000; Belgium, 67,500; Holland, 55,000; Italy, 32,000 in 1903, 38,000 in 1906, 51,000 in 1908, 36,000 in 1909, 50,000 in 1910; Sweden, 35,000; Denmark, 22,500; Spain, 18,000; Roumania, 13,000; Servia, 3300; Bulgaria, 1700; Switzerland, 950.

To give an idea of the progress made by the beet-sugar industry during the last 50 years, the production of raw sugar in the two countries where this industry has developed most is given in the following table:

	In France	In Germany	Germany	
			Yield of sugar per 100 kilos beet	Annual consumption per head
	Tons	Tons		
1840	22,784	14,200	5·9 kilos	2·5 kilos
1850	62,165	53,300	7·3 ,,	3·1 ,,
1860	126,480	126,520	8·6 ,,	4 3 ,,
1870	282,136	186,000	8·6 ,,	4·7 ,,
1890	750,000	1,336,000	12·5 ,,	8·5 ,,
1903	1,080,000	1,921,000	14·4 ,,	13 ,,
1905	—	1,605,000	14·9 ,,	14·9 ,,
1906	730,000	2,400,000	14·7 ,,	17 0 ,,
1909	807,500	2,037,400	16·3 ,,	19·5 ,,

The production in France varies, since the agriculturists require as much as 3*s.* per 100 kilos of beet. While the *consumption* was 40,000 tons in 1887 and 527,000 in 1902, it rose to 600,000 tons in 1908, owing to the modification of the fiscal conditions of 1903–1904. The number of workpeople occupied for about two months was 38,000 in 1908, with an average wage of 3*s.* per day. The area under beet in France in 1907 was 210,000 hectares.

Some of the large factories in France and Belgium have diffusion plants in the middle of the beet-growing districts, the sugar juices after treatment with lime being forced through pipes, often several kilometres long, to the factories, where they are further worked up.

In 1906 England imported 1,583,000 tons of sugar, and in 1909 about 940,000 tons of refined and 815,000 tons of raw sugar. In 1910 the imports were 98,000 tons of raw sugar and 84,400 tons of refined sugar, the total value being £24,554,000; the exports were 31,000 tons. The United States imported 2,095,000 tons of raw sugar and 76,000 tons of refined sugar in 1910, and 2,049,000 tons (£19,873,600) of raw and 160,000 tons of refined sugar in 1911.

In Germany the beet-sugar industry has reached its greatest perfection and magnitude, and from 1880 to 1902 Germany was the largest exporter (as much as two-thirds of its own output). In 1909–1910, in spite of the diminution of exports resulting from the Brussels Convention,[1] Germany exported 423,000 tons of refined sugar and 310,000 tons of the

[1] The Fiscal System in Germany from 1841 to 1866 was based on the quantity of beets, the object being to bring about improvements in the cultivation of the beet and hence increase in the sugar-content; the tax corresponded with about 18*s.* per quintal, and was refunded to the manufacturer for all exported sugar. From 1870 to 1886 the tax was 1*s* 7*d.* per quintal of beet, it being assumed that 12 5 kilos of beet were required to give

raw product, the home consumption being 1,260,000 tons. The exports were 740,000 tons in 1890, 883,000 in 1904, and 1,145,000 in 1906. In 1908–1909, 358 factories and 39 refineries were working in Germany. Certain German factories, employing 46 workmen, treat 4000 to 5000 quintals of beet, but in Italy many more employees are required. In 1909–1910 Germany produced 10,600,000 tons of beet, but in 1910–1911 only 5,200,000 tons.

In Austria large batteries of diffusors are used and a more complete exhaustion is obtained even at a lower temperature; in general, indeed, the modern plants are more perfect than those in Germany. In 1908 Austria-Hungary exported 610,000 tons of refined and 195,000 of raw sugar.

The following Table shows, for different countries: I, manufacturing tax in pence per kilo; II, retail price in pence per kilo; III, mean annual consumption in kilos per head in 1899 and 1909; IV, mean quintals of beet produced per hectare in 1908–1910; V, kilos of refined sugar obtained from 100 kilos of beet; and VI, kilos of refined sugar from 1 hectare.

	I	II	III		IV	V	VI
			1899	1909			
England . . .	0·96	5·3	40	41·1	—	—	—
United States . .	0·96	4·8	28·4	37·2	220	12·44	2706
Switzerland . .	0·67	4·8	25·7	30·2	—	—	—
Denmark . .	0·575	6·7	21·6	35·5	287	13·82	3950
Sweden and Norway .	2·88	7·7	15·7	{24·5 / 17·8}	266	14·26	3803
Germany . . .	1·92	6·2	13·7	19·7	284	16·35	4809
Holland . . .	5·47	9·6	13	19·8	257	14·80	3803
France . . .	2·6	7·2	12·8	16·9	265	13·03	3445
Belgium . . .	1·92	6·7	10·5	15·1	281	14·37	4032
Austria-Hungary .	3·45	8·15	8·3	11·2	249	15·74	3909
Russia . . .	2 7	8·25	6	9·1	136	16·37	2230
Spain . . .	0·77	8·15	4·5	5·4	289	11·88	3439
Portugal . . .	—	—	6	6·2	—	—	—
Greece . . .	2·4	8·15	3	3·8	—	—	—
Roumania. . .	—	—	3·5	4·1	165	14·53	2392
Turkey . . .	5·47	9·6	3·5	5·7	—	—	—
Italy . . .	6·7	14·4	2·8	3·9	299	11·27	3378
Servia . . .	3·17	7·7	3	3·5	—	—	—

The influence of the price of sugar on the consumption is shown not only by the above Table but also by the following significant facts: when the manufacturing tax was reduced by 40 per cent. in France in 1903–1904, the consumption increased by 61 per cent.; in Germany a 33 per cent. reduction in the taxation produced an increase of about 60 per cent. in the consumption, and in Belgium 55 per cent. more sugar was consumed as a result of the lowering of the tax by 29 per cent.

In Italy the sugar industry has developed only within the last fifteen years (*see* p. 477), as is shown by the Table on p. 481 (in 1906 the 39,500 hectares under beet gave a mean yield of 270 quintals of beet per hectare, the limits being 328 and 177).

1 kilo of sugar; but even in 1870 1 kilo of sugar could be obtained from 11·9 kilos of beet, and in 1887 from 8 1 kilos. But since the exports increased enormously and the taxes refunded remained the same, the manufacturers enjoyed indirectly a considerable export bounty, which diminished the Exchequer receipts from £3,000,000 to less than £760,000 (1888). A modification was hence made in the system of taxation, sugar produced and consumed at home paying a tax of £1 per quintal, while that exported was freed from tax and received a bounty of 2*s.* 6*d.* (raw) or 3*s.* 6*d.* (refined) per 100 kilos (1896–1903). Further, the import duty was left at £2 per quintal, so that German producers were allowed to sell their sugar at high prices at home (even during the abundance of 1900–1901) and to employ part of their profits to lower the price of sugar sold abroad in competition with other countries. After the Brussels Convention, however, export bounties ceased and the import duty was reduced, to 5*s.* + 16*s.* (manufacturing tax in Germany). Under these new conditions, the exports diminished somewhat, but the home consumption increased owing to the lowered prices. The wholesale price in 1910 was £2 per quintal (that of sugar for export, without tax, being 19*s.*); the retail price was 14*d.* per kilo in 1875, 7*d.* in 1902, and 6*d.* in 1910. The German Government received £5,750,000 in sugar taxes in 1900–1901 and almost £8,000,000 in 1909–1910.

Year	Output of raw sugar	Imported raw sugar	Total consumption of refined sugar	Remarks
	Tons	Tons	Tons	
1887 . .	184	140,000	125,500	100 tons of raw sugar taken as 90 tons of refined
1889 . .	632	78,000	71,000	
1894 . .	2,090	75,000	70,000	
1897 . .	3,336	75,500	71,000	
1901 . .	73,800	37,100	99,880	
1902 . .	95,166	20,000	100,000	
1903 . .	128,000	5,200	120,000	Overproduction of 25,000 tons
1904 . .	79,000	2,100	73,000	
1905 . .	112,000	5,100	112,000	
1906 . .	136,000	15,000 (?)	138,245	Mean yield of refined sugar from the beets, 11·86 per cent., the mean content being 13·56 per cent.; loss in working, 1·70 per cent.
1906–1907 .	106,400	23,738 (?)	—	
1907–1908 .	136,000	4,903	145,000	

The Italian Government received £60,000 in manufacturing tax and £2,680,000 in import duty in 1897, about £2,560,000 in tax and £320,000 in Customs duty in 1903, £3,920,000 in tax and £66,060 in Customs duty in 1909–1910. The production of beets in Italy was 1,256,660 tons in 1909 and 1,679,070 tons in 1910, the output of sugar being 161,600 tons in 1908–1909, 107,200 tons—from 9,670,700 quintals of beet—in 1909–1910, and 170,000 tons in 1910–1911. In 1910 Italy imported 5800 tons of first-grade and 655 tons of second-grade sugar.

DETERMINATION OF SUGAR-CONTENT. Sugar is estimated in various ways. With an aqueous sugar solution, the content of saccharose can be determined by means of the specific gravity at 17·5°, compared with water at 17·5°, this being measured by hydrometers, pyknometers, &c. (*see* vol. i, p. 72). In the factory, use is generally made of a hydrometer (*saccharometer*), which, at 17·5°, gives directly the percentage of saccharose present.

These saccharometers were first proposed by Balling and were subsequently corrected by Brix, degrees Brix expressing the percentage of sugar. In France and Belgium, and sometimes also in Germany, saccharometers gauged at 15° and referred to water at 15° are used, and the Berlin Royal Commission for the control of standards prescribed the use of saccharometers giving the density of solutions at 20° referred to that of water at 4°.

The following Table gives the densities and degrees Brix (grammes of sugar per 100 grms. of solution) for the temperature 17·5°, and also, for each 10°, the values from the other two Tables, so that the intermediate values in these two Tables can be calculated roughly. The saccharometer is read with the precautions and in the manner indicated on p. 74 of vol. i and on p. 147 of this volume. The Table gives densities above 66° Brix, which cannot be determined by hydrometers, but which serve to calculate the degree of purity of impure saccharine solutions (molasses, &c.; *see later*).

MATEGCZEK AND SCHEIBLER'S TABLE, GIVING THE SPECIFIC GRAVITIES AND DEGREES BRIX OF SACCHARINE SOLUTIONS

Sp. gr. at $\frac{17\cdot5°}{17\cdot5°}$	Degrees Brix	Sp. gr. at $\frac{17\cdot5°}{17\cdot5°}$	Degrees Brix	Sp. gr. at $\frac{17\cdot5°}{17\cdot5°}$	Degrees Brix	Sp. gr. at $\frac{17\cdot5°}{17\cdot5°}$	Degrees Brix	Sp. gr. at $\frac{17\cdot5°}{17\cdot5°}$	Degrees Brix
1·00388	1	1·08778	21	1·18460	41	1·29531	61	1·42258	81
1·00779	2	1·09257	22	1·18981	42	1·30177	62	1·42934	82
1·01173	3	1·09686	23	1·19505	43	1·30777	63	1·43614	83
1·01570	4	1·10145	24	1·20033	44	1·31381	64	1·44298	84
1·01970	5	1·10607	25	1·20565	45	1·31989	65	1·14986	85
1·02373	6	1·11072	26	1·21100	46	1·32601	66	1·45678	86
1·02779	7	1·11541	27	1·21639	47	1·33217	67	1·46374	87
1·03187	8	1·12013	28	1·22182	48	1·33836	68	1·47074	88
1·03599	9	1·12488	29	1·22728	49	1·34460	69	1·47778	89
1·04014	10	1·12967	30	1·23278	50	1·35088	70	1·48406	90
1·04027 $\left[\frac{15°}{15°}\right]$	10	1·12999 $\left[\frac{15°}{15°}\right]$	30	1·23330 $\left[\frac{15°}{15°}\right]$	50	1·35182 $\left[\frac{15°}{15°}\right]$	70	1·48716 $\left[\frac{15°}{15°}\right]$	90
1·038143 $\left[\frac{20°}{4°}\right]$	10	1·126984 $\left[\frac{20°}{4°}\right]$	30	1·229567 $\left[\frac{20°}{4°}\right]$	50	1·347174 $\left[\frac{20°}{4°}\right]$	70	1·479976 $\left[\frac{20°}{4°}\right]$	90
1·04431	11	1·13449	31	1·23832	51	1·35720	71	1·49199	91
1·04852	12	1·13934	32	1·24390	52	1·36355	72	1·49915	92
1·05276	13	1·14423	33	1·24951	53	1·36995	73	1·50635	93
1·05703	14	1·14915	34	1·25517	54	1·37639	74	1·51359	94
1·06133	15	1·15411	35	1·26086	55	1·38287	75	1·52087	95
1·06566	16	1·15917	36	1·26658	56	1·38939	76	1·52810	96
1·07002	17	1·16413	37	1·27235	57	1·39595	77	1·53550	97
1·07441	18	1·16920	38	1·27816	58	1·40254	78	1·54290	98
1·07884	19	1·17430	39	1·28400	59	1·40918	79	1·55040	99
1·08329	20	1·17943	40	1·28989	60	1·41586	80	1·55785	100
1·08354 $\left[\frac{15°}{15°}\right]$	20	1·17985 $\left[\frac{15°}{15°}\right]$	40	1·29056 $\left[\frac{15°}{15°}\right]$	60	1·41628 $\left[\frac{15°}{15°}\right]$	80	1·56165 $\left[\frac{15°}{15°}\right]$	100
1·080959 $\left[\frac{20°}{4°}\right]$	20	1·176447 $\left[\frac{20°}{4°}\right]$	40	1·286456 $\left[\frac{20°}{4°}\right]$	60	1·411715 $\left[\frac{20°}{4°}\right]$	80	1·551800 $\left[\frac{20°}{4°}\right]$	100

If the degrees Brix are read with solutions at temperatures other than the normal, corrections must be made by means of the following Tables :

STAMMER'S TABLE FOR REDUCING TO 17·5° DEGREES BRIX READ AT DIFFERENT TEMPERATURES

Temperature		Degrees Brix of the Solutions											
		5	10	15	20	25	30	35	40	50	60	70	75
13°	These corrections to be subtracted from the observed Brix degrees	0·18	0·19	0·21	0·22	0·24	0·26	0·27	0·28	0·29	0·33	0·35	0·39
15°		0·11	0·12	0·14	0·14	0·15	0·16	0·17	0·17	0·17	0·19	0·21	0·25
17°		0·02	0·03	0·03	0·03	0·04	0·04	0·04	0·04	0·04	0·05	0·05	0·06
18°	These corrections to be added to the observed Brix degrees	0·03	0·03	0·03	0·03	0·03	0·03	0·03	0·03	0·03	0·03	0·03	0·02
19°		0·08	0·08	0·09	0·09	0·10	0·10	0·10	0·10	0·10	0·10	0·08	0·06
21°		0·20	0·22	0·24	0·24	0·25	0·25	0·25	0·26	0·26	0·25	0·22	0·18
23°		0·32	0·35	0·37	0·38	0·39	0·39	0·39	0·40	0·42	0·39	0·36	0·33
25°		0·44	0·47	0·49	0·51	0·53	0·54	0·55	0·55	0·58	0·54	0·51	0·48

Example.—If a sugar solution shows 40° Brix (*i.e.* 40 per cent. of sugar) at a temperature of 23°, 0·4 must be added to reduce the reading to the true Brix degrees at 17° ; so that 40 + 0·4 = 40·4 degrees Brix at 17°.

SCHEIBLER'S TABLE SHOWING DEGREES BRIX AT 15° AND THE CORRESPONDING DEGREES AT OTHER TEMPERATURES (FROM 10° TO 25°)

Temperature	DEGREES BRIX OR PERCENTAGE OF SUGAR											
10° . .	5·15	10 19	15 22	20 24	25 27	30 29	35 30	40·31	50·33	60 35	70·36	75·36
12° . .	5 10	10 12	15 14	20·15	25 17	30 18	35 18	40 19	50 20	60 21	70 21	75·21
14° . .	5 04	10 04	15 05	20 05	25 06	30 06	35 06	40 07	50 07	60 07	70 07	75·07
15° . .	5 00	10 00	15 00	20·00	25 00	30·00	35 00	40 00	50 00	60 00	70 00	75·00
17° . .	4 92	9 91	14·90	19 89	24 88	29 87	34 37	39 87	49 86	59 86	69 86	74·86
19° . .	4 83	9 80	14 78	19·77	24 75	29 74	34 73	39·73	49 72	59·71	69 71	74·71
21° . .	4·72	9·69	14 66	19 64	24 62	29 60	34 59	39 59	49 57	59 57	69·57	74·57
23° . .	4 61	9·57	14·53	19 50	24 48	29 46	34 45	39·44	49·42	59 42	69 42	74·42
25° . .	4 49	9 44	14·40	19 36	24·34	29 32	34·30	39 29	49·27	59·27	69 27	74·28

Example.—If a solution reads 19·36° Brix at a temperature of 25°, this would correspond with 20° Brix at the normal temperature of 15°. For intermediate values, either of temperature or of concentration, the corresponding results are easily obtained by interpolation. Thus, 18° Brix at temperature 15° would give, at other temperatures, values higher than those corresponding with 15° Brix by three-fifths of the difference between the values in the 15° Brix and 20° Brix columns. So that a solution showing 18° Brix at the temperature 15° would show, at the temperature 17°, $14{\cdot}90 + \frac{3}{5}(19{\cdot}89 - 14{\cdot}90) = 14{\cdot}90 + 2{\cdot}99 = 17{\cdot}89°$ Brix.

In the quantitative determination of sugar, use is commonly made of its action on polarised light (*see* pp. 26 and 330), this being measured in the *polarimeter*. The rotatory power of a sugar solution is proportional to the concentration and almost independent of the temperature. In these determinations it is necessary to use pure sugar solutions, decolorised by means of a little basic lead acetate, which precipitates the albuminoids, colouring-matters, and other impurities; the filtered solution is examined in the polarimeter. If the saccharose is accompanied by another optically active sugar—for instance, glucose (dextro-rotatory)—allowance must be made for the rotation of the latter. In such a case the diminution in rotation produced by inversion of the saccharose with dilute acid would give the amount of this sugar.

POLARIMETERS AND SACCHARIMETERS.[1] One of the best-known polarimeters is the Laurent shadow instrument (Fig. 351), which contains, in place of the compensator

[1] It has been mentioned already (*see* p 26) that crystals of Iceland spar and quartz have the property of decomposing a ray of light into two polarised rays, the ordinary and the extraordinary. If a prism of Iceland spar with length greater than the breadth, with its acute angle of 68°, is cut diagonally and lengthwise so as to divide it into two rectangular triangular prisms (Fig 350), and these be cemented together again with Canada balsam, the result is a Nicol prism. When a ray of light, *lm*, enters the *nicol*, of the two refracted rays (*mo*, *mp*), the ordinary one, *mo*, is totally reflected by the layer of Canada balsam and is thrown out of the crystal (*or*), whilst the extraordinary ray, *mp*, passes through the prism (*pqs*) and emerges polarised. This ray is able subsequently to traverse a second nicol only when the principal section of this *analysing nicol* is parallel to that of the first *polarising nicol*. If, on the other hand, the two principal sections are perpendicular, the ray undergoes total reflection and will not pass through the second nicol; in intermediate positions, varying quantities of light are allowed to pass. If a layer of water is placed between the perpendicular nicols, still no light will pass through the analyser. But if a sugar solution is interposed, the light passes with a greater or less intensity through the analyser, which must be rotated through a certain angle (proportional to the quantity of sugar) to produce total disappearance of the light. In order to determine exactly when the luminous ray is extinguished (even in this case a kind of half-shadow is always observed), Soleil attempted to divide the luminous field into two halves with complementary colours. Indeed, if a ray of polarised light is passed through a quartz plate placed

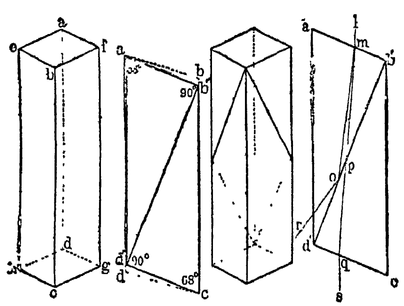


FIG. 350.

and double-polarisation quartz plate, a special semicircular quartz plate, *D*, half a wave-length in thickness and occupying one-half of the field. The polariser, *B*, is rotated by means of the rod, *X*, and the rotation which restores the two halves of the field to the same luminosity is indicated on a graduated circle, *C*, provided with a vernier, read by means of the lens, *N*, and illuminated by the mirror, *M*.

The source of monochromatic light is a double Bunsen flame coloured with sodium chloride, the light being collected by the lens, *B*, and the observation made through the eye-piece, *O*. The scale of the apparatus is regulated by the screw, *Z*, so that it reads zero when the two halves of the field are equally illuminated. If a tube containing a liquid, interposed between the two nicols, causes the right-hand half of the field to darken, the liquid is dextro-rotatory, while darkening of the left-hand half indicates a lævo-rotatory compound. From the rotation read on the scale, the specific rotation can be calculated by the formulæ given on p. 27.

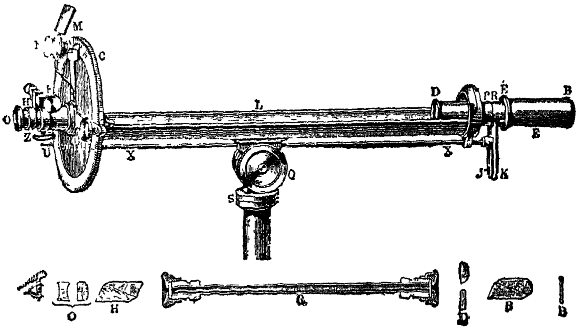


FIG. 351.

The practical examination of sugars is made with polarimeters furnished with special scales and known as *saccharimeters ;* the Laurent polarimeter has a saccharimetric graduation as well as that showing circular degrees.

In the French saccharimeters (Soleil and Laurent) the 100 division corresponds with a normal aqueous solution of pure saccharose (obtained by precipitation of a very concentrated aqueous solution with alcohol and drying at 60° to 70°) containing 16·350 grms. in 100 c.c. at 17·5°, the reading being made in a tube 20 cm. long (the same reading is given by a quartz plate 1 mm. in thickness). In the German instruments (Ventzke-Scheibler, Schmidt and Haensch) the 100 reading is obtained with a length of 20 cm. of a saccharose solution of sp. gr. 1·1, which contains 26·048 grms. per 100 c.c. at a temperature of

between the two nicols, one half of this plate being dextro- and the other lævo-rotatory, and the junction of the two lying exactly on the axis of the light, the two halves of the field will appear illuminated with complementary colours. If the plate is 3·75 mm. in thickness and the analyser is rotated through 24·5°, the two halves of the field are almost completely extinguished and assume a pale red coloration, similar in the two halves. But if a sugar solution is interposed, the two halves assume different colours, extinction being restored by rotation of the analysing nicol. Later Soleil suggested compensating the rotation of the sugar solution by introducing,

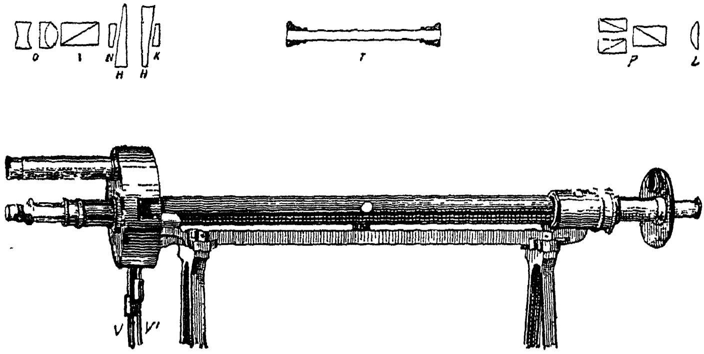


FIG. 352.

to a greater or less extent, between the nicols, a conical quartz plate or *compensator*, moved by a rack indicating on a scale the thickness of the plate and hence the equivalent rotation. The more modern saccharimeters of the Soleil-Ventzke type have two compensators, each formed of two quartz wedges (MN and HK, Fig. 352) of opposite rotations, and are fitted also with the Lippich *polariser* formed of three nicols (*P*), which give a field divided into three zones; when these zones are not equally illuminated, the two lateral ones show a colour different from that of the middle one. The analyser is enclosed in a metal box to protect it from dust. The two compensators with their scales are regulated by two screws, *V* and *V'*. When the two scales indicate zero, the three zones should be equally illuminated.

17·5°.[1] So that a reading of one division corresponds with 0·26048 grm. of saccharose per 100 c.c., or 1 grm. of sugar per 100 c.c. gives a reading of 3·839 divisions.

The source of light for modern saccharimeters is an incandescent gas-burner enclosed in a blackened metal chimney fitted with a ground-glass window, or an incandescent electric lamp of at least 32 candle-power with a ground-glass globe and also enclosed in a black case. In order that the apparatus may not become heated, the lamp should be placed at a distance of about 15 cm., and to render the luminous fields more distinct the light is passed first through a glass cell with parallel walls filled with 6 per cent. bichromate solution in a layer 15 mm. thick; in this way the more refractive rays are absorbed and a uniform yellow light obtained. The normal tube of the saccharimeter contains a layer of liquid exactly 20 cm. long, but for very dilute and slightly rotating solutions tubes of 30, 40, and 50 cm. are used, whilst for solutions which are not quite colourless tubes of 10 or 5 cm. may be employed; in all cases the readings are referred to the normal length of 20 cm. Some tubes are provided with an aperture for the introduction of a thermometer, so that the temperature of the solution may be read in the instrument.

The saccharimeter scale extends from 0 to 100 divisions on the positive side and to − 30 on the negative side. The integral divisions are given by the zero of the vernier, *N* (Fig. 353), and the decimal parts by that division of the vernier scale which coincides exactly with a division on the scale; in Fig. 353 the reading is + 2·6 divisions.[2]

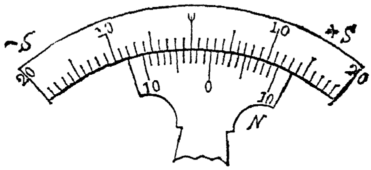


FIG 353.

The specific rotatory power of saccharose varies little with the concentration (up to 30 per cent.) and with the temperature (between 15° and 25°), but it is best to work near to 20°, when $[\alpha]_D^{20} = + 65·5°$.[3]

[1] That is, in 100 Mohr c.c., 1 Mohr c.c. being the volume of 1 grm. of water at 17·5° weighed in air with brass weights. The *true* c.c. is the volume of 1 grm. of water at 4° weighed *in vacuo*; calculation on the basis of the coefficient of expansion of water shows that 100 Mohr c.c. are equal to 100·234 true c.c., so that 100 *true* c.c. of the normal saccharose solution at 17·5° would contain 25·987 grms. of saccharose. The International Commission for uniform methods of sugar analysis proposed in 1900 the fixing of the 100 point of the saccharimeter by a length of 20 cm. of a solution obtained by dissolving 26 grms. of pure saccharose in water to a volume of 100 *true* c.c. at 20° and polarising at 20° (100 true c.c. of water at 20° weigh 99·7174 grms. in air and 99·8294 grms. *in vacuo*).

[2] With double compensation saccharimeters (furnished with two scales, a *working* scale and a *control*, *V* and *V′*, Fig. 352) the procedure is as follows: When the tube with the sugar solution is introduced between the nicols the control scale is placed at zero, the working scale being then moved by the screw until the field is uniformly illuminated and its position read. The sugar solution is next removed and the control scale moved until the field is again uniform, the reading of this scale being nearly equal to the first reading of the working scale. The tube of solution is now again introduced and the position of the working scale, near to the zero-point, read after its adjustment to give uniform luminosity. Finally the tube is again removed and the control scale moved until the field is uniform and its position read. The final result is obtained by subtracting the mean of the second pair of readings from the mean of the first pair. Thus, if the readings were + 78·6, + 78·4, + 0·2, and − 0·3, the result would be 78·5 − 0·05 = + 78·45.

[3] *Invert sugar*, on the contrary, has a rotatory power varying markedly with the concentration and temperature. A solution of saccharose containing the normal weight (26·048 grms.) contains, after inversion, 27·419 grms. of invert sugar, and if this is contained in 100 c.c. it gives a deviation of − 32·66 in a 20 cm. tube at 20°. The variation per degree of temperature is 0·5, so that at 0° this reading would be − 42·66 and, in general, at any temperature, *t*, it would be − 42·66 + 0·5 *t*. If no account is taken of variations due to the concentration, 1 division Ventzke corresponds with 0·8395 grm. of invert sugar in 100 c.c. (Mohr), the solution being read in a 20 cm. tube at 20°; or 1 grm. of invert sugar dissolved in 100 Mohr c.c. gives a reading of − 1·191 division. The specific rotatory power of invert sugar for different concentrations (from 1 to 35 per cent.) is given by the formula: $[\alpha]_D^{20} = - 19·657 - 0·03611c$, *c* indicating the weight of invert sugar in 100 c.c. For concentrations near 15 per cent. the value − 20·2 may be taken for the specific rotation of invert sugar, 1 *circular* degree then corresponding with 2·475 grm. of invert sugar in 100 true c.c. and 1 grm. of invert sugar in 100 true c.c. giving a rotation in circular degrees of − 0·404.

Glucose has a specific rotation, $[\alpha]_D^{20} = + 52·8°$, which is constant after *muta-rotation* has ceased (*see* p. 27), *i.e.* if the observation is made after the solution has been either left for 24 hours or boiled for 15 minutes. The concentration and the temperature have virtually no influence on the rotatory power and, with a 20 cm. tube, 1° corresponds with 0·947 grm. in 100 true c.c. and hence 1 grm. of glucose in 100 true c.c. will give a rotation of 1·056°. One division on the Ventzke saccharimeter corresponds with 0·3448° (corrected for the dispersion), and the normal weight is 32·71 grms. of glucose in 100 Mohr c.c.; thus 1 Ventzke division, with a 20 cm. tube and a temperature of 20° corresponds with 0·3271 grm. of glucose per 100 Mohr c.c., or 1 grm. of glucose per 100 Mohr c.c. gives a rotation of 3·057 Ventzke divisions.

For *fructose* (*levulose*) the data are uncertain owing to the difficulty of obtaining pure crystals, and the rotatory power varies with the concentration (for solutions of about 10 per cent. strength, $[\alpha]_D^{20} = - 93°$) and with the temperature (an increase of 1° of temperature diminishes the specific rotatory power by 0·67°). One division on the Ventzke saccharimeter corresponds with 0·1838 grm. of levulose in 100 Mohr c.c., or 1 grm. of levulose gives a rotation of − 5·439 Ventzke divisions in a 20 cm. tube at the temperature 20°.

Lactose. For $C_{12}H_{22}O_{11} + H_2O$, after the disappearance of the muta-rotation, the specific rotation, which is

CHEMICAL DETERMINATION OF SUGARS. With the exception of saccharose and raffinose, the sugars (glucose, levulose, &c.) reduce Fehling's solution (an alkaline solution of copper sulphate containing salts of organic hydroxy-acids; *see* pp. 212 and 335) in the hot, with separation of a corresponding amount of cuprous oxide. Fehling's solution is obtained by mixing, just before using, equal volumes of the two following solutions: (*a*) 69·278 grms. of pure crystallised copper sulphate ($CuSO_4 + 5H_2O$), air-dried until constant in weight, dissolved in water to 1 litre; (*b*) 346 grms. of Rochelle salt (sodium potassium tartrate) and 100 grms. of pure solid sodium hydroxide dissolved in water to 1 litre. Since saccharose does not reduce Fehling's solution, it must be first inverted. For this purpose, 9·5 grms. of the sugar are dissolved in 700 c.c. of N/5-hydrochloric acid and the solution heated for 30 minutes in a water-bath at 75°, neutralised with caustic soda, and made up to 1 litre. This solution, which contains 10 grms. of invert sugar, is then ready for testing.

The Fehling test may be either volumetric or gravimetric, the concentration of the sugar being reduced to about 1 per cent. (by a preliminary trial) and the details of the procedure being followed exactly. *Volumetric method:* 40 c.c. of water and 10 c.c. of Fehling's solution (5 c.c. of each of the component solutions) are brought to boiling in an Erlenmeyer flask, a measured quantity (4 to 5 c.c.) of the sugar solution run in from a burette, and the liquid again heated and kept boiling for a definite time (2 minutes for glucose or invert sugar, 4 minutes for maltose, and 6 for lactose); the flame is then removed, a few drops of the liquid filtered, and the filtrate acidified with a little acetic acid and tested with a drop of potassium ferrocyanide solution. If a red coloration is produced, the test is repeated with a larger quantity of sugar solution, whilst if no red coloration appears, a less quantity of the sugar is tried. This procedure is continued until in the last two tests, representing excess and deficiency of the sugar solution, the difference between the two volumes is not more than 0·1 c.c.; the mean of these two volumes is employed in calculating the sugar-content of the solution. 100 c.c. of undiluted Fehling's solution, under the above conditions, correspond with 0·4945 grm. of glucose, 0·533 of levulose, 0·515 of invert sugar, 0·740 of maltose, and 0 676 of lactose (hydrated).

The *gravimetric estimation* is carried out as follows (Allihn's method): To 60 c.c. of Fehling's solution, diluted with 60 c.c. of boiled distilled water and heated to boiling, are added 25 c.c. of the sugar solution of about 1 per cent. concentration, the liquid being then again heated and kept boiling for a definite time (2 minutes for glucose, levulose, and invert sugar, 4 for maltose, and 6 for lactose). The solution is then filtered at once, with the aid of a filter-pump, through a dried and weighed Soxhlet tube containing a layer of asbestos, the cuprous oxide being repeatedly washed with a total quantity of 300 to 400 c.c. of boiling water, then with two or three portions of alcohol, and finally with ether. The tube is then dried in an oven, and the cuprous oxide subsequently reduced to metallic copper by passing a current of dry hydrogen through the tube and gently heating the oxide with a small flame; the hydrogen is kept passing until the tube is quite cold, when the weight is taken. From the weight of copper thus obtained, the

but slightly influenced by the concentration, is $[\alpha]_D^{20} = +52\ 53°$; this diminishes by 0·075° for every degree rise in temperature. One degree of rotation corresponds with 0 9519 grm. of lactose in 100 true c c., so that 1 grm. of lactose gives a rotation of 1·051°. For the Ventzke saccharimeter, the normal weight is 32 95 grms. per 100 Mohr c.c. (32·83 grms. in 100 true c.c.), so that 1 Ventzke division in a 20 cm. tube corresponds with 0·3295 grm. of lactose in 100 Mohr c.c. and 1 grm. of lactose in 100 Mohr c.c. gives a rotation of 3 035 Ventzke divisions.

Maltose has a specific rotation (after muta-rotation has been destroyed; *see* Glucose) varying with the temperature and concentration according to the equation: $[\alpha]_D^t = 140\ 375 - 0\ 01837\,c - 0{\cdot}095\,t$, where t indicates the temperature and c the percentage by weight of anhydrous maltose. For medium concentrations, $[\alpha]_D^{20} = +138{\cdot}2°$ and 1° corresponds with 0 3618 grm. of maltose per 100 true c c. with a 20 cm. tube and 1 grm. of maltose in 100 c.c. gives a rotation of 2 764°. For the Ventzke saccharimeter, the normal weight is 12 55 grms of maltose in 100 true c.c or 12·58 grms. in 100 Mohr c.c., and for a 20 cm. tube at the temperature 20°, 1 Ventzke division corresponds with 0 1255 grm. of maltose in 100 true c.c., while 1 grm. of maltose in 100 true (Mohr) c.c. gives a rotation of 7 968 (7 949) Ventzke divisions.

Raffinose, $C_{18}H_{32}O_{16} + 5H_2O$, has the specific rotation, $[\alpha]_D^{20} = +104{\cdot}5°$, which is almost independent of the temperature and concentration; for anhydrous raffinose the value is + 123·15°. One degree of rotation corresponds with 0 4785 grm. of hydrated raffinose in 100 true c.c. with a 20 cm. tube and 1 grm. of raffinose in 100 true c.c. gives a rotation of 2 09°. For the Ventzke saccharimeter the normal weight is 16 576 grms. per 100 Mohr c.c. or 16·537 grm. per 100 true c.c., so that 1 Ventzke division corresponds with 0·16576 grm. of raffinose in 100 Mohr c.c. and 1 grm. of raffinose in 100 Mohr c.c. gives a rotation of 6·033 Ventzke divisions in a 20 cm. tube.

corresponding weight of sugar is read off from the following Table, all the numbers representing milligrams:

Copper	Glucose	Invert sugar	Maltose	Lactose	Copper	Glucose	Invert sugar	Maltose	Lactose	Copper	Glucose	Invert sugar	Maltose	Lactose
30	16	—	25·3	—	155	79·1	81·6	135·9	112·6	280	145·5	151·9	247·8	208·3
35	18·5	—	29·6	—	160	81·7	84·3	140·4	116·4	285	148·3	154·9	252·2	212·3
40	20·9	—	33·9	—	165	84·3	87·0	144·9	120·2	290	151·0	157·8	256·5	216·3
45	23·4	—	38·3	—	170	86·9	89·7	149·4	123·9	295	153·8	160·8	261·1	220·3
50	25·9	—	42·6	—	175	89·5	92·4	153·8	127·8	300	156·5	163·8	265·5	224·4
55	28·4	—	47·0	—	180	92·1	95·2	158·3	131·6	305	159·3	166·8	269·9	228·3
60	30·8	—	51·3	—	185	94·7	97·8	162·7	135·4	310	162·0	169·7	—	232·2
65	33·3	—	55·7	—	190	97·3	100·6	167·2	139·3	315	164·8	172·7	—	236·1
70	35·8	—	60·1	—	195	100·0	103·4	171·6	143·1	320	167·5	175·6	—	240·0
75	38·3	—	64·5	—	200	102·6	106·3	176·1	146·9	325	170·3	178·6	—	243·9
80	40·8	—	68·9	—	205	105·3	109·1	180·5	150·7	330	173·1	181·6	—	247·7
85	43·4	—	73·2	—	210	107·9	111·9	185·0	154·5	335	175·9	184·7	—	251·6
90	45·9	46·9	77·7	—	215	110·6	114·7	189·5	158·2	340	178·7	187·8	—	255·7
95	48·4	49·5	82·1	—	220	113·2	117·5	193·9	161·9	345	181·5	190·8	—	259·8
100	50·9	52·1	86·6	71·6	225	115·9	120·4	198·4	165·7	350	184·3	193·8	—	263·9
105	53·5	54·8	91·0	75·3	230	118·5	123·2	202·9	169·4	355	187·2	196·8	—	268·0
110	56·0	57·5	95·5	79·0	235	121·2	126·0	207·4	173·1	360	190·0	199·8	—	272·1
115	58·6	60·1	99·9	82·7	240	123·9	128·9	211·8	176·9	365	192·9	203·0	—	276·2
120	61·1	62·8	104·4	86·4	245	126·6	131·8	216·3	180·8	370	195·7	206·1	—	280·5
125	63·7	65·5	108·9	90·1	250	129·2	134·6	220·8	184·8	375	198·6	209·2	—	284·8
130	66·2	68·1	113·4	93·8	255	131·9	137·5	225·3	188·7	380	201·4	212·4	—	289·1
135	68·8	70·8	117·9	96·6	260	134·6	140·4	229·8	192·5	385	204·3	215·5	—	293·4
140	71·3	73·5	122·4	101·3	265	137·3	143·2	234·3	196·4	390	207·1	218·7	—	297·7
145	73·9	76·1	126·9	105·1	270	140·0	146·1	238·8	200·3	395	210·0	221·8	—	302·0
150	76·5	78·9	131·4	108·8	275	142·8	149·0	243·3	204·3	400	212·9	224·9	—	306·3

NON-SUGAR, APPARENT DENSITY, TRUE DENSITY, AND QUOTIENT OF PURITY. Sugars and their solutions are distinguished, commercially and industrially, by their content of saccharose, water, and *solids not sugar* (*e.g.* salts and various organic substances).

The Brix saccharometer is graduated with pure sugar solutions, and hence gives results which are increasingly inaccurate as the degree of impurity of the sugar solutions increases. *Apparent density* is that shown by the Brix hydrometer, while the *real density* corresponds with the true content of sugar determined by direct analysis (by the polarimeter or, after inversion, by Fehling's solution). The difference between the real and apparent densities, expressed in degrees Brix, indicates the *non-sugar* in Brix degrees, while the *ratio* between the real and apparent densities, in degrees Brix, is termed the *quotient of purity* and, when multiplied by 100, shows the percentage of sugar present independently of the water.

In the *analysis of a mixture of various sugars* a number of optical and chemical tests must be made in order to deduce, directly or indirectly, the quantities of the separate components (*see* Villavecchia, *Chim. Anal. Tecnol.*, vol. ii, pp. 223 *et seq.*).[1]

[1] If only saccharose and another sugar are present, p grms. of the mixture are dissolved in water to 100 c c. and the polarisation, P, read; if a_1 is the rotation of 1 grm. of saccharose per 100 c.c. and a_2 that of 1 grm. of the other sugar, the quantities x and y of saccharose and the other sugar respectively are given by the formulæ (I) $x = \frac{P - a_2 p}{a_1 - a_2}$, (II) $y = \frac{a_1 p - P}{a_1 - a_2}$, since $x + y = p$ (III) and $a_1 x + a_2 y = P$ (IV). The values of a_1, a_2, and P must be given their proper algebraic signs (+ or −).

A. In the special case of a *mixture of saccharose and glucose*, the components x and y may be determined in various ways:

(1) The glucose (y) may be estimated by means of Fehling's solution; formula IV then gives $x = \frac{P - a_2 y}{a_1}$ (V). Since saccharose reduces Fehling's solution to a very slight extent, small proportions of glucose are best determined by means of Soldaini's reagent, which consists of 150 grms of potassium bicarbonate, 104·4 grms. of normal potassium carbonate, and 100 c.c. of the copper sulphate solution used for Fehling's solution, made up to a litre with water.[*]

(2) The solution of the mixture is polarised (P), the saccharose being inverted and the polarisation again read (P_1). If a_3 is the rotation of 1 grm of invert sugar (= − 1 191), then, since 1 grm. of saccharose gives 1 053 grm. of invert sugar, we have $1{\cdot}053\ a_3 x + a_2 y = P_1$ (VI) and hence $x = \frac{P - P_1}{a_1 - 1{\cdot}053 a_3}$ (VII) and $y = \frac{a_1 P_1 - 1{\cdot}053 a_3 P}{a_2(a_1 - 1{\cdot}053 a_3)}$ (VIII) a_1 having the value 3 839 and a_2, 3 057, it follows that $x = \frac{P - P_1}{5{\cdot}093}$ (IX) and $y = \frac{3{\cdot}839 P_1 + 1{\cdot}254 P}{5{\cdot}093 \times 3{\cdot}057}$ (X), which are the quantities of the two sugars in p grms. of the mixture. The

The total *ash* of a sugar is determined by weighing 3 grms. into a tared platinum dish, moistening it with a few drops of concentrated sulphuric acid, carbonising over a Bunsen flame and incinerating in a muffle at a low red heat (about 700°) so that the ash does not fuse. From the sulphated ash, one-tenth of its weight is deducted in order to correct for the increase due to the formation of sulphates. By means of tables the quantity of *soluble ash* can also be deduced.

The water is determined by heating 5 to 10 grms. of the sugar in a flat glass dish covered with a clock-glass at 105° to 110° first for 2 hours and subsequently to constant weight. Subtraction from 100 of the water and the sugar gives the percentage of *total non-sugar*, while further subtraction of the ash gives the *organic non-sugar*. The *alkalinity* of the sugar is determined by titrating an aqueous solution of 20 grms. of the product with decinormal sulphuric acid in presence of phenolphthalein; the result is calculated as grammes of CaO per 100 grms. of sugar.

percentages will therefore be $\frac{100x}{p}$ and $\frac{100y}{p}$ respectively. For a mixture of *saccharose* and *levulose*, $a_2 = -5{\cdot}439$, so that $y = \frac{-3\ 839P_1 - 1\ 254P}{27{\cdot}701}$; for *saccharose* and *invert sugar*, $a_2 = -1{\cdot}191$ and the denominator becomes 6·066 instead of 27·701; for *mixtures of saccharose and maltose*, $a_2 = 7\ 949$ and $y = \frac{3\ 839P_1 + 1{\cdot}254P}{5{\cdot}093 \times 7{\cdot}949}$; for *saccharose* and *lactose hydrate*, $a_2 = 3\ 035$.

(3) The glucose is first determined by means of Fehling's solution; in another portion of the solution the saccharose is inverted and the reducing sugars again estimated with Fehling's solution; the difference between these two estimations gives the invert sugar and this, multiplied by 0 95, the saccharose.

B. With a *mixture of saccharose and raffinose*, the polarisation is determined before (P) and after (P_1) inversion; a_1 and a_2 being the known rotations of 1 grm. of each of the two sugars and a_3 and a_4 those of 1 grm of the respective inverted products, it follows that. $a_1x + a_2y = P_1$ (XIII) and $1{\cdot}053\ a_3x + 1{\cdot}036\ a_4y = P_1$ (XIV); substitution in these of the values $a_1 = 3\ 839$, $a_2 = 7{\cdot}11$, $1\ 053\ a_3 = -1\ 254$ and $1\ 036\ a_4 = 3\ 643$ gives $x = \frac{0\ 5124P - P_1}{3{\cdot}2211}$ and $y = \frac{1\ 254P + 3{\cdot}839P_1}{22\ 9}$. For the determination of the raffinose by means of methylphenylhydrazine, in presence of saccharose and invert sugar, *see* Raffinose, p. 442.

C When two reducing sugars, but neither saccharose nor raffinose is present, it is sufficient to measure the polarisation and apply formulæ I to IV. But if a non-saccharine substance is also present, it is necessary to determine also the number (F) of c c of Fehling's solution reduced by a weight, p, of the substance; if b_1 and b_2 are the volumes (c.c) of Fehling's solution reduced by 1 grm. of each of the two sugars dissolved in 100 c c., then: $a_1x + a_2y = P$ (XV) and $b_1x + b_2y = F$ (XVI) and hence $x = \frac{b_2P - a_2F}{a_1b_2 - a_2b_1}$ and $y = \frac{a_1F - b_1P}{a_1b_2 - a_2b_1}$. With a *mixture of glucose and levulose*, $a_1 = 3{\cdot}057$, $a_2 = -5\ 439$, $b_1 = 202\ 4$, and $b_2 = 186$, so that $x = \frac{186P + 5\ 439F}{1669}$ and $y = \frac{3\ 057F - 202{\cdot}4P}{1669}$. For *mixtures of glucose and maltose*, a_2 has the value 7·940 and b_2 135; these last two numbers hold also for mixtures of *invert sugar and maltose*, but then $a_1 = -1\ 191$ and $b_1 = 194$; for *mixtures of glucose and lactose*, $a_1 = 3\ 057$, $a_2 = 3\ 035$, $b_1 = 202{\cdot}4$, and $b_2 = 148$, while for *invert sugar* and *lactose*, a_2 and b_2 have the values just given, but $a_1 = -1\ 191$ and $b_1 = 194$.

D. With a *mixture of saccharose* (x), *glucose* (y), *and levulose* (z), if a weight, p, is dissolved to 100 c c., and a_1, a_2, a_3, a_4 represent the respective rotations of 1 grm. of each of these sugars and of invert sugar in 100 c.c., b_2 and b_3 the number of c c. of Fehling's solution reduced by 1 grm. of each of the reducing sugars, P and P_1, the polarisations before and after inversion, and F the number of c.c. of Fehling's solution reduced by weight p of the substance, then (XVII) $P = a_1x + a_2y + a_3z$, $P_1 = 1\ 053\ a_4x + a_2y + a_3z$; $F = b_2y + b_3z$. The first two of these give $x = \frac{P - P_1}{a_1 - 1\ 053a_4}$, which corresponds with formula VII. Then (XVIII) $a_2y + a_3z = P - a_1x$ and $b_2y + b_3z = F$, which are analogous to formula XV, allow of the determination of the values of y and z. Thus $x = \frac{P - P_1}{5\ 093}$ and for y and z we have, in analogy to formula XVI (diminishing the polarisation, P, by the rotation of the saccharose, $3{\cdot}839x$), $y = \frac{233P + 714P_1 + 27{\cdot}7F}{8500}$ and $z = \frac{15\ 57F - 254P - 777P_1}{8500}$. With a *mixture of saccharose* (x), *invert sugar* (y) *and lactose* (z), the saccharose is arrived at as above, and then:

$$y = \frac{15\ 46F - 185\ 6P - 568P_1}{3896} \quad \text{and} \quad z = \frac{6{\cdot}066F + 243P + 745P_1}{3896}.$$

Practical Examples. 26·048 grms. of the sugar or mixed sugars are dissolved in a 100 c.c. flask and, if the solution is coloured, basic lead acetate solution (10 to 30 drops) is added drop by drop until it forms no further turbidity; the solution is made up to 100 c c. with water, filtered through a dry filter and polarised in a 20 cm. tube. a drop of acetic acid being previously added, if necessary, to make the liquid clearer.

If it is thought desirable to eliminate the excess of lead acetate, the liquid is made up to volume with saturated sodium sulphate solution instead of with water.

In the case of a mixture of invert sugar and saccharose, if the normal weight solution gives a rotation of + 24·0 before and − 27·0 after inversion, the quantity of saccharose in 100 c.c. of the solution will be $\frac{24 + 27}{5\ 093} = 10\ 01$, and that of invert sugar $\frac{3\ 839 \times 27 - 1{\cdot}254 \times 24}{6{\cdot}066} = 12\ 12$ grms.

If other sugars are also present, the invert sugar is first determined with Fehling's solution, such quantity of the sugar solution being taken (after a preliminary trial) as contains about 0 2 grm of invert sugar and the determination being made with 50 c c. of Fehling's solution by the gravimetric method. The result is subject to a *slight* correction, according to a Table by Meissl and Hiller, for the influence of the saccharose on the Fehling's solution; but this only in cases where the invert sugar is present in relatively small proportion compared with the saccharose, as, for instance, when samples of saccharose are being analysed.

PURIFICATION OF WASTE-WATERS FROM SUGAR-WORKS. The waters requiring purification, since they are highly contaminated and readily ferment, are those used in emptying and washing the diffusors, those from the pulp-presses and, partly, those in which the beets have been washed. The first contain up to 0·5 per cent. of suspended matter and 0·6 to 0·8 per cent. of dissolved organic matter, with about 0·3 per cent. of sugar; they have a bad smell, and it is usually prohibited to introduce them as they stand into streams.

Chemical purification (with lime or iron oxide or sulphate) is costly and insufficient, while the mechanical method of filtration to remove the suspended matter does something but only partially solves the problem. Biological purification (*see* vol. i, p. 223), preceded by filtration or by aeration (omitting the septic tank) gives better results than the older processes, but is not entirely satisfactory (it eliminates 40 to 70 per cent. of the organic matter). The principal bacteria which destroy saccharose are *Leuconostoc* and *Clostridium*. The problem of the complete purification of these waste-waters still remains unsolved.

D. TETROSES

MANNOTETROSE, $C_{24}H_{42}O_{21}$, is found in manna, and yields 2 mols. galactose, 1 of fructose, and 1 of glucose on hydrolysis.

E. HIGHER POLYOSES

These are not, or but slightly, sweet, and are amorphous and, in some cases, insoluble in water. On hydrolysis they usually give either pentoses alone or hexoses alone, pentoses and hexoses being formed together only in rare instances. Their molecular weights are unknown, but their molecules are very large and are represented by the general formula, $n\ (C_6H_{12}O_6) - (n - 1)\ H_2O$; where n is very large, this approximates to $(C_6H_{10}O_5)_n$, which represents the results of analysis.

F. HIGHER POLYOSES

Starch, Dextrin, Gum, Glycogen, Cellulose

STARCH, $(C_6H_{10}O_5)_x$. It has already been pointed out (pp. 111 and 429 how starch originates in vegetable organisms and how it passes from the leaves, where it is formed under the influence of chlorophyll and of light, to the reserve stores of the plants (tubers, seeds, &c.; in cryptogams, which have no chlorophyll, starch is not formed). It is a carbohydrate, and occurs in white granules insoluble in both cold and hot water, although with the latter it swells up, forming *starch paste*, which is coloured a characteristic deep blue by dilute iodine solution. Starch paste is dissolved by acids, forming glucose (*see* p. 434), and by diastase (*see* pp. 111, 116, and 168), forming intermediate polyoses with less complex molecules (dextrins) and then maltose and isomaltose. Starch does not give the reactions of the monoses (*i.e.* with Fehling's solution, phenylhydrazine, &c.), and hence contains no free carbonyl groups, so that its rational formula (*see* pp. 438, 441, and 442) will be: $(C_6H_{10}O_5\cdot O)$ . . . $(C_6H_{10}O_4\cdot O\cdot C_6H_{10}O_4)$ . . . $(O\cdot C_6H_{10}O_5)$, where there is only one dicarbonyl linking, possibly in the middle; two such linkings are inadmissible, since otherwise decomposition should give, together with d-glucose, another substance with two carbonyl groups. Such a substance has, however, never been obtained.

The molecular weight has not been established, but it must be very high, and, according to Syniewski, the formula is $C_{216}H_{360}O_{180}$, the molecule consisting of twelve C_{18} nuclei.

The shape of the starch granules varies with the plant from which they are obtained, so that it is possible to ascertain the origin of starch by observing it under the microscope (with a magnification of 200 diameters; *see* Figs. 354

to 361).[1] When examined in polarised light, between crossed nicols, potato-starch granules, having a stratified structure and an eccentric nucleus, show a black cross like the multiplication sign (×) (Fig. 362), while other stratified starch granules with a central nucleus also behave like doubly refracting crystals but show a black cross more like the sign of addition (+) ; this is seen well with wheat starch (Fig. 363). Starch granules show their stratification better under the microscope if they are treated with a dilute solution of chromic acid containing a little sulphuric acid, and in some cases dark radial striæ also appear.

Commercially the name *flour* is given to starches from cereals, leguminoseæ, acorns, chestnuts, &c., and that of *starch* to those from potatoes, manihot root, arrowroot, palm stems, sago, &c., but chemically there is no difference. The flour of these plants contains more or less gluten (wheat, 12 per cent. ; rice, 3 to 5 per cent.), and wheat yields 55 to 65 per cent. of starch ; maize, 60 to 65 per cent. ; rice, 70 to 73 per cent. ; rye, 45 per cent. ; oats, 32 per cent. ; barley, 38 per cent. ; beans, peas, and lentils, 38 per cent.[2]

The specific gravity of potato starch, when air-dried, is 1·5029, and when dried at 100°, 1·6330.

When heated above 160° it is transformed into dextrin.

Manufacture. In Italy starch is extracted principally from rice, maize, &c., but in Germany almost exclusively from potatoes. A starch factory should always have a supply of pure cold water, not very hard and free from iron.

Fresh mature potatoes contain about 20 per cent. of starch (minimum 18 per cent., maximum 21 per cent.), the proportion being determined sufficiently exactly by a very rapid physical process, proposed in 1837 by Berg, applied in 1845 by Balling, and improved in 1880 by Behrend, Märcker, and Morgen. An exact relation exists between the specific gravity of potatoes and their starch-content, and it has been found that the difference between the total dry substance (S) and the starch-content (F) is constant (the proportion of *non-starch*, N, is on the average 5·752 per cent.). So that a determination of the dry matter gives the proportion of starch, since $F = S - N$. Further, if the relation between F and the specific gravity is determined once for all, a Table[3] can be prepared showing the proportion of dry matter or of starch from the specific gravity, which can be determined from the loss in weight of a given weight of potatoes in air (5 kilos) when weighed immersed in water ; if, for instance, this weight is 400 grms., the loss of weight will be 4600 grms. and the specific gravity 5000 : 4600 = 1·087, which the Table shows to correspond with

[1] Different kinds of starch may possess granules of similar form, but can be distinguished by the varying mean magnitudes of the granules, although in most kinds there are a greater or less number of granules much smaller than the average, these being sometimes grouped together in ovoidal or bunch-like masses (e.g. rice, oat, starch, &c.). The average sizes of the granules of the different starches, in micromillimetres (μ), are generally as follow :

(1) Wheat . large granules, 26–29μ, more common ; small granules, 7μ
(2) Barley : ,, ,, 20μ, ,, ,, ,, ,, 4·5μ
(3) Rye : ,, ,, 36μ, ,, ,, ,, ,, 6μ
(4) Potato : ,, ,, 60–80μ, ,, ,, ,, ,, 20μ
(5) Rice : bunches, 20μ, of several granules ; separate granules, 5μ
(6) Oats : ,, 30μ, ,, ,, ,, ,, 8μ
(7) Maize : large granules, 18–20μ, more common ; small granules, 5μ
(8) Buckwheat : ,, ,, 9μ (polyhedra) ,, ,, 5μ

The mean percentage compositions of potatoes, wheat, and rice are as follow

	Water	Starch	Non-nitrogenous extractives	Cellulose	Fat	Proteins	Ash
Potatoes . . .	76	18·7	1	0·8	0·2	2·1	1·2
Wheat	13·5	64	3·8	2·5	2·0	12·5	1·7
Rice	13·1	76·8		0·6	0·6	7·8	1·0

[3] *See* p. 492.

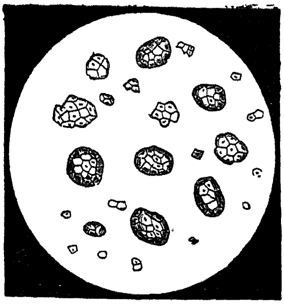


FIG. 354.—Rice starch.

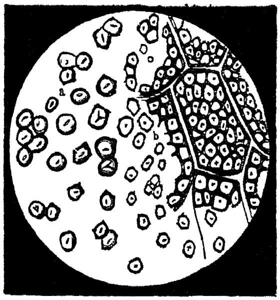


FIG. 355.—Maize starch.
(*a*) Free granules; (*b*) horny part

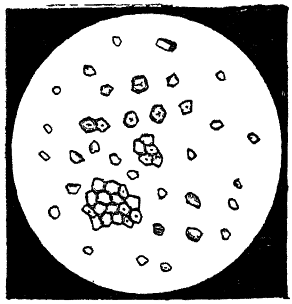


FIG. 356.—Buckwheat.

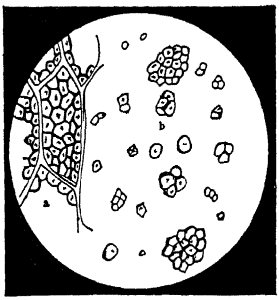


FIG. 357.—Oat starch.
(*a*) Cellular tissue; (*b*) free granules.

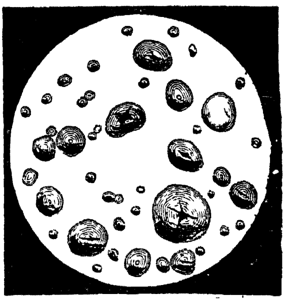


FIG. 358.—Rye starch

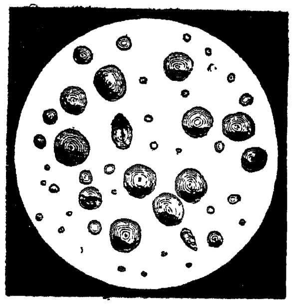


FIG. 359.—Wheat starch.

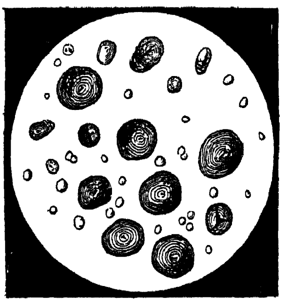


FIG. 360.—Barley starch.

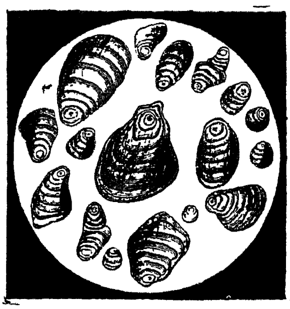


FIG. 361.—Potato starch.

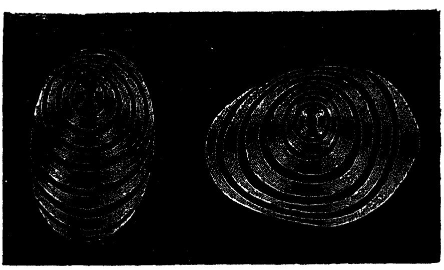


FIG. 362.—Potato starch in polarised light.

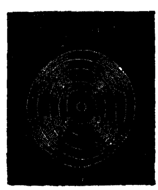


FIG. 363.—Wheat starch in polarised light.

21·2 per cent. of dry matter and 15·4 per cent. of starch. By means of the balance shown in Figs. 364 and 365 or of the Reimann or Schwarzer basket steelyard the potatoes can be rapidly weighed in air and in water at 17·5°. To calculate the practical yield the value given in the Table should be diminished by 1·5 per cent., since part of the starch is converted during extraction into soluble sugar, which may also exist to a small extent in potatoes which are either not too ripe or too old. The washing of potatoes in starch factories is *most* important, and is carried out in machines of various types. The first washing, to

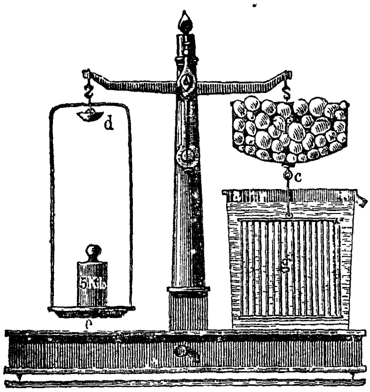


FIG. 364.

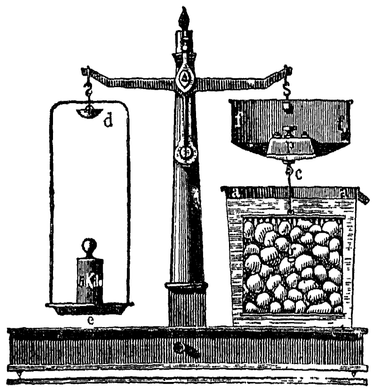


FIG. 365.

remove the soil and stones, which are present to the extent of about 8 per cent., can be done in the machine shown in Fig. 103 (p. 118) or in transporter channels like those used for sugar-beets (*see* Fig. 293 p. 449). The potatoes are then raised by an inclined Archimedean screw in a perforated channel (*see* Fig. 295, p. 450), the washing being repeated with copious jets of water in a long vessel having a concave perforated bottom and fitted with vaned stirrers, which are sometimes furnished with brushes (Siemen's washer, Fig. 366). The potatoes pass along the vessel in the opposite direction to that taken by the water, which is introduced clean at the extremity where the washed potatoes emerge. The washing of 400 quintals of potatoes per 24 hours requires, on an average, 20 cu. metres of water per hour.

The *rasps* used to convert the potatoes into pulp, by rupturing all the starch-containing cells, consist of a number of saw-edged steel plates fixed radially round a drum which has

Weight in water of 5 kilos of potatoes, grms.	Specific gravity	Dry matter, per cent.	Starch, per cent.	Weight in water of 5 kilos of potatoes, grms.	Specific gravity	Dry matter, per cent	Starch, per cent.	Weight in water of 5 kilos of potatoes, grms	Specific gravity	Dry matter, per cent.	Starch, per cent.
375	1 080	19 7	13 9	480	1·106	25 2	19 4	585	1·132	30·8	25·0
380	1 081	19 9	14·1	485	1·107	25 5	19 7	590	1 134	31 3	25 5
385	1 083	20 3	14 5	490	1·109	25 9	20·1	595	1·135	31·5	25·7
390	1 084	20 5	14·7	495	1 110	26·1	20·3	600	1·136	31 7	25 9
395	1 086	20 9	15·1	500	1 111	26·3	20·5	605	1 138	32 1	26 3
400	1 087	21 2	15·4	505	1 112	26·5	20 7	610	1 139	32 3	26 5
405	1 088	21 4	15 6	510	1·113	26 7	20 9	615	1 140	32·5	26 7
410	1·089	21 6	15·8	515	1·114	26·9	21 1	620	1·142	33 0	27·2
415	1·091	22 0	16 2	520	1 115	27 2	21·4	625	1 143	33·2	27 4
420	1 092	22 2	16 4	525	1·117	27·6	21 8	630	1·144	33·4	27·6
425	1 093	22 4	16 6	530	1·119	28 0	22 2	635	1 146	33·8	28·0
430	1 094	22 7	16 9	535	1·120	28·3	22 5	640	1·147	34·1	28 3
435	1 095	22 9	17 1	540	1·121	28 5	22·7	645	1·148	34·3	28·5
440	1·097	23 3	17 5	545	1 123	28 9	23 1	650	1 149	34 5	28·7
445	1·098	23 5	17·7	550	1·124	29 1	23 3	655	1 151	34·9	29 1
450	1·099	23 7	17 9	555	1 125	29 3	23·5	660	1·152	35 1	29·3
455	1·100	24 0	18·2	560	1·126	29 5	23 7	665	1 153	35 4	29·6
460	1 101	24 2	18 4	565	1·127	29·8	24 0	670	1·155	35·8	30·0
465	1·102	24 4	18 6	570	1·129	30 2	24 4	675	1 156	36·0	30·2
470	1·104	24·8	19 0	575	1·130	30·4	24 6	680	1·157	36 2	30·4
475	1·105	25·0	19·2	580	1·131	30 6	24·8	685	1 159	36·6	30·8

a diameter of 50 to 60 cm. (Figs. 367 and 368) and rotates at a speed of 800 to 1000 revolutions per minute. The Angele rasp (Fig. 369) consists of such a drum working in a cylindrical casing, which in some forms has a saw-toothed inner surface (Schmidt rasp, Fig. 370), the potatoes from the feeder being forced against the drum by means of an adjustable

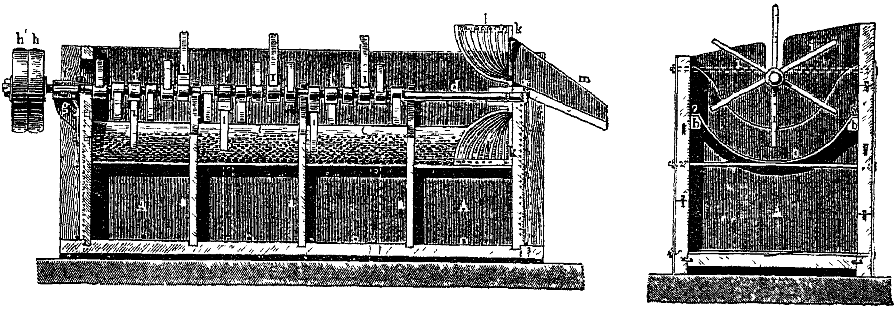
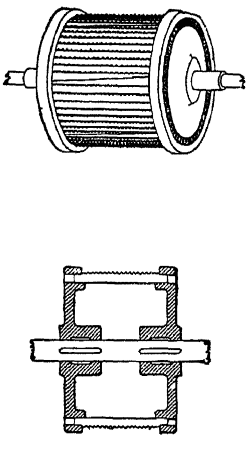


FIG. 366.



FIGS. 367 AND 368.

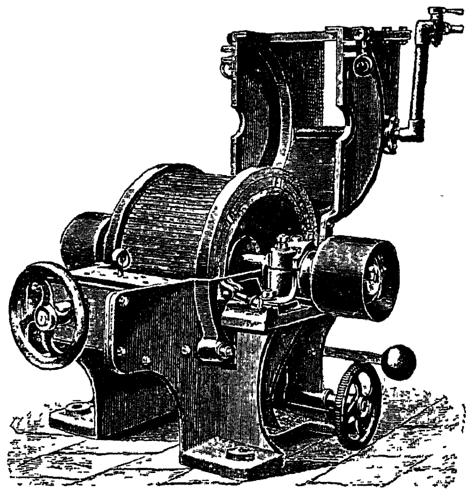


FIG. 369.

wooden compressor, *A*, and the resulting pulp drawn between the two indented surfaces. A powerful water-jet keeps the saw-edges clean and washes the pulp into a tank underneath. The pulp from which the starch has been removed (100 quintals of potatoe. give 3 to 4 quintals of dried residues) still contains unaltered starchy cells, and as a loss of 2 to 3 per cent. of starch would thus result, the pulp is passed into ordinary horizontal stone mills like those used in flour-mills, the stones having a diameter of about a metre and making 150 turns per minute. The Champonnois rasp, used in France, is composed of a drum, *E* (Figs. 371 and 372), formed of a number of saw-blades with the teeth turned inwards; the washed potatoes enter by the feeder, *J*, and are forced against the saw-edged periphery by the blades, *F*, which are rapidly rotated by the pulley, *H*. A water-jet supplied at *K* washes the pulp between the saw-blades into the vessel, *N*, below, loss by spurting being prevented by the casing, *M*.

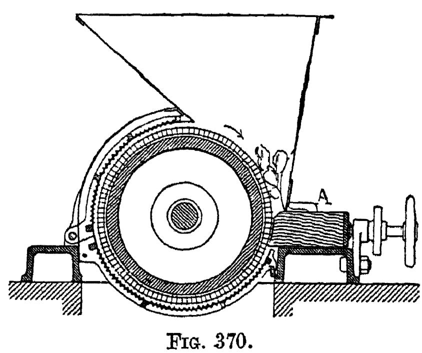


FIG. 370.

For large factories, however, Uhland has suggested the replacement of the mill by a special machine which completely disintegrates the remaining starch-containing cells

without rupturing the fibres. This machine consists of a horizontal cone of cast-iron, either channelled or edged (Figs. 373 and 374) and enclosed in a casing of similar shape; by means of a screw regulator, *V*, the distance between the cone and casing can be varied.

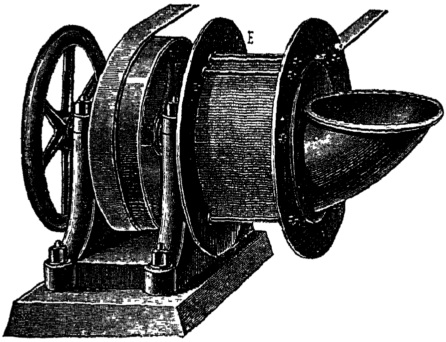


FIG. 371.

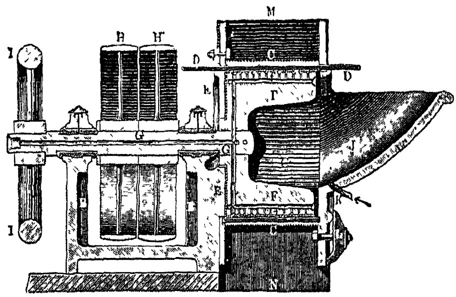


FIG. 372.

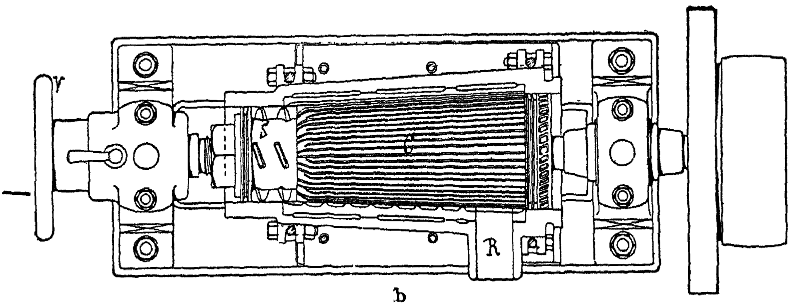


FIG. 373.

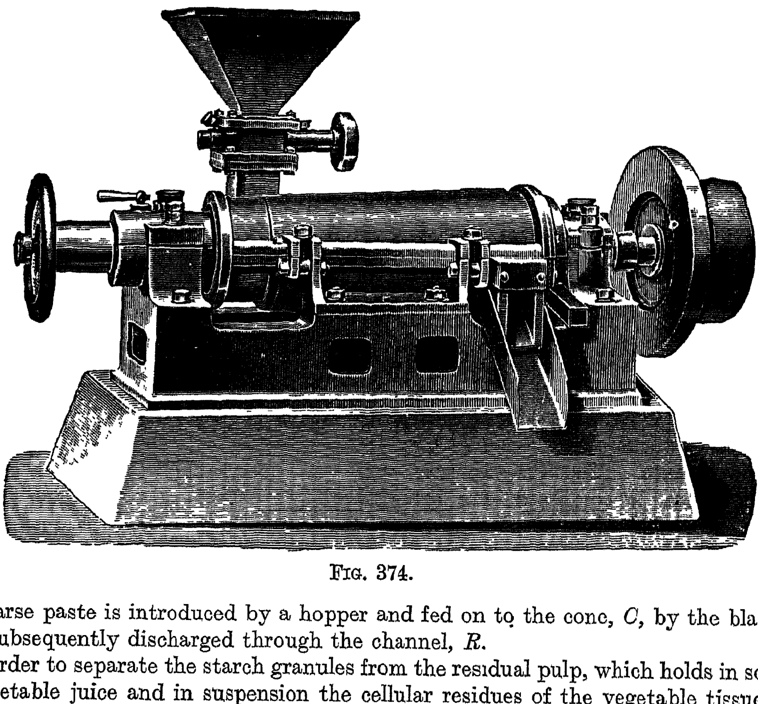


FIG. 374.

The coarse paste is introduced by a hopper and fed on to the cone, *C*, by the blades, *S*, being subsequently discharged through the channel, *R*.

In order to separate the starch granules from the residual pulp, which holds in solution the vegetable juice and in suspension the cellular residues of the vegetable tissues, epidermis, &c., the pulp is passed immediately (to avoid fermentation) on to copper sieves

of various types (usually semi-cylindrical and several metres in length); these retain the residues, while a water-spray, helped by suitable scrapers, carries the starch granules through the meshes (*see* transverse section, Fig. 375); these same scrapers, which are arranged helically, carry the exhausted residues to the far end of the sieve and keep the latter clean.

When these operations are carried out properly and in large works, the total loss is not more than 0·3 kilo of dry starch on 100 kilos of washed potatoes; these losses are detected by estimating chemically the starch in the ultimate exhausted residues.

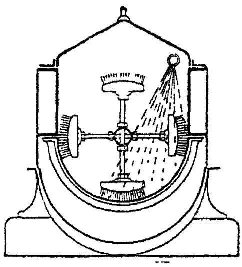


Fig. 375.

The milky liquid collected under the sieves also contains, in addition to starch, small proportions of colouring and gummy matters, proteins, dextrin, and very fine particles of epidermis, sand, &c. In order to separate these impurities, the starch-milk is introduced into large concrete vessels, where the sand separates in a few minutes. The liquid with the suspended starch is then removed to another vessel, where the whole of the starch separates after a rest of 10 to 12 hours. But in some cases the starch is subjected to levigation with a gentle current of water in a number of vessels, in which the starch forms successive deposits. The water and the dissolved impurities are readily separated, either during or after standing, by means of a floating syphon consisting of a funnel joined to an india-rubber tube (Fig. 376). The volume of the deposit tanks is taken to be about 1 cu. metre per quintal of potatoes treated.

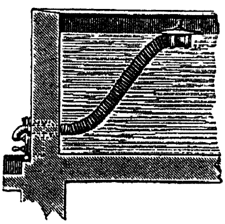


Fig. 376.

In some starch factories the starch is still separated from the milky liquid by a kind of levigation on inclined planes, the liquid passing slowly along large wooden or cement channels, 30 metres long, 1 to 3 metres wide, 50 to 60 cm. deep, and with a slope of 3 to 5 mm. per metre. The coarser starch, together with a little sand, is deposited in the first parts of the channel; then comes the best starch, while the smallest granules, mixed with a few organic impurities, are the last to settle. The water which emerges from the end of the channel is passed through two or three depositing tanks before being rejected. In order that the working may be continuous, two channels are always employed, one being in use while the starch is being removed from the other. The channels are fed from large reservoirs provided with stirrers so that the density of the starch suspension may be kept constant and uniform (3° Bé., the liquid being fed at the rate of 6 litres per minute per 2·5 sq. metres of channel surface). The crude starch from the first and last portions of the channel may be purified by repeating the levigation. But that obtained from depositing tanks forms a compact mass composed of a lower layer of coarse granules mixed with a little sand, an intermediate purer layer, and a grey uppermost layer mixed with organic detritus. It is indispensable to wash the starch quickly, as in time the impurities impart to it a pale yellow colour. For this purpose the layer of starch—the so-called *green starch* (*i.e.* impure, moist starch)—is covered with double its depth of water, a suspended stirrer fitted with long blades (Fig. 377) being then lowered to the surface of the starch; the first more impure layer is thus stirred up so as to form a dense milk of 4° to 5° Bé., this being deposited in an adjacent wooden vat or on the inclined channel. The middle purer layer is then stirred up and the suspension removed, and so on.

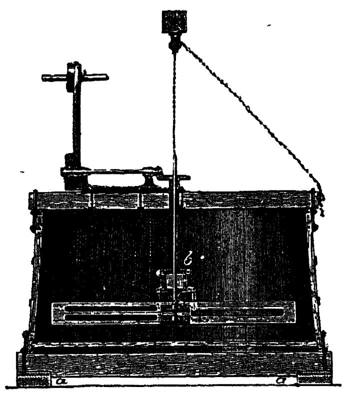


Fig. 377.

In these wooden vats (*see* Fig. 377) the stirring is repeated, this operation being continued until a perfectly white starch is obtained, the wash-waters being removed after each deposition.

When the starch is not refined in this way and dried, the growth of mould is prevented by keeping it under water slightly acidified with sulphuric acid until it is to be sold. This green starch, which is used, for example, for manufacturing glucose, contains about 50 to 55 per cent. of water; part of this can be removed in centrifuges similar to those used for sugar (p. 469), the perforated drum being coated inside with a fine cloth to retain the granules. The superficial layer of the cake of starch is scraped off, as it contains impurities, and the remainder (with 35 to 40 per cent. of moisture) then discharged below; with a drum 80 cm. in diameter 50 kilos of starch are obtained. The centrifuges are fed with a dense suspension of the starch of 20° Bé. The impure grey starch obtained in the secondary sedimentation vessels is mixed to a dense milk and passed through fine silk sieves, which retain the detritus and solid proteins, &c., the sieved milk being conveyed to other finer sieves and then to the inclined channels or sedimentation vats. To prevent bacterial action and to increase the whiteness of starch, 0·5 kilo or more of calcium bisulphite solution (in some cases sulphurous acid is used) is sometimes added to each cubic metre of the milk. These reagents, as well as sulphuric acid or caustic soda in small proportions, facilitate the deposition of the starch in the tanks, but they impart a faint reaction to the final starch, and it is advisable to employ them only in the treatment of frozen or bad potatoes, where the product readily ferments and turns yellow. Bleaching is sometimes effected with dilute, filtered calcium hypochlorite solution (1 : 300), together with sulphuric acid; after a few minutes contact, the starch is washed in an abundant supply of cold water until the reaction of the chlorine disappears. The last trace of yellow in the starch can be corrected by slight blueing with ultramarine, indigo carmine, Prussian blue, &c.

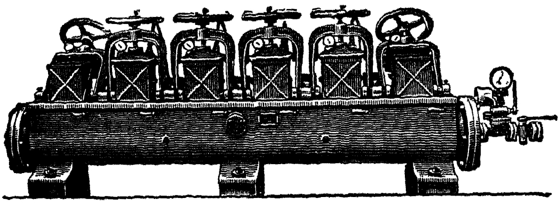


FIG. 378.

When potato or cereal starch is to be prepared in cubical or similar cakes, the mass from the sedimentation tanks is introduced into moulds of galvanised or tinned iron with

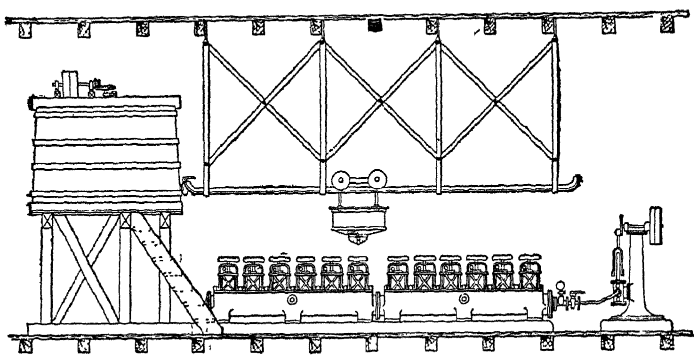


FIG. 379.

perforated bases (the cubes are 16 cm. in each direction); these are either enclosed in evacuated cases or, as Uhland suggested, subjected to considerable air-pressure, so as to remove the water as far as possible (*see* Fig. 378). Fig. 379 shows how the batteries of moulds are arranged in large factories; the dense starch-cream from the vat fills a hopper travelling on a suspended iron rail and stopping above each mould to fill it; when all the moulds are full, they are closed hermetically and the air-compressor started. With a suitable machine the smooth cakes are removed whole from the moulds, and as they contain very little water, the time required for drying is considerably shortened.

Modern plants make use of another arrangement devised by Uhland (Fig. 380). Here the moulds are fitted inside with a rubber bag with a perforated base and covered with cloth; this fits closely to the walls and gives a purer starch, while the moulds can be thoroughly cleaned after each operation.

The *drying* of the starch is carried out in hot-air desiccators, which readily reduce the moisture to 20 per cent., which is the customary proportion ; if more moisture is present an allowance is made to the purchaser, but if there is less than 20 per cent. the seller loses, as no allowance is then made. In order to obtain starch of good appearance the temperature of drying should be about 30° to 35° (at 50° it begins to swell and form lumps) and the air should issue from the desiccator almost saturated with moisture after traversing all the frames or gratings on which the moist starch is spread in a thin layer or in cakes. The best arrangement consists of channels or galleries 10 to 12 metres long, 1·2 metre wide, and 2 metres high, through which trolleys carrying the frames pass from one end to the other ; the hot, dry air is injected under slight pressure in the opposite direction by a large helical fan, gentle suction being applied at the far end if necessary. Rapid drying depends not so much on the temperature as on the supply of the proper amount of pure, dry air. The doors of the drying tunnel slide up and are opened just sufficiently to allow of the entry and exit of the trolleys from time to time (every hour).

It has recently been proposed to employ mechanical dryers consisting of a number of stories fitted with endless bands, or of long revolving cylinders, while in some cases drying in a vacuum has been practised as with distillery residues (*see* Fig. 149, p. 154), time and space being thus economised and the output consequently greatly increased.

The dried starch forms friable lumps, and to obtain it in powder it is passed first into grooved cylinders and then into sieves similar to those employed in mills. For the use of ball-mills, *see* vol. i, pp. 512 and 588. Statistics, *see later*. Microscopical examination, *see* p. 491.

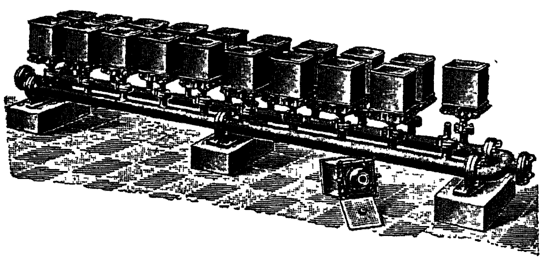


FIG. 380.

Yield of Starch and Treatment of Residues. Of 20 kilos of starch present in potatoes, 17 to 18 are usually obtained in the pure, dry state, the rest going into the residues. The moist pulp, freed from starch (within 0·5 per cent.), contains the parenchyma and epidermis of the potatoes, which are composed largely of cellulose saturated with aqueous juices. The pressed pulp (about 16 per cent. of the weight of the potatoes), which is sometimes dried (it then constitutes 3 to 4 per cent. of the weight of the potatoes and contains 50 to 60 per cent. of starch), forms a good cattle-food, either alone or mixed with bran, chaff, &c. It is dried in the vacuum apparatus used for " grains " (*see* p. 154) or for beet-pulp (*see* Fig. 309, p. 455). The waste waters contain potash salts (0·06 per cent. K_2O + 0·017 per cent. P_2O_5 + 0·1 per cent. ash + 0·24 per cent. sugar + 0·12 per cent. gum + 0·17 per cent. nitrogenous substances) and may be used for irrigating pasture land ; if it is not digested quickly it undergoes fermentation. These waters are readily clarified by colloidal aluminium hydroxide. The moist, non-pressed pulp has the following percentage composition : water, 86 ; protein, 0·7 to 0·9 ; fat, 0·1 ; starch and extractives, 11·2 ; cellulose, 1·5 ; ash, 0·4.

WHEAT STARCH. Since wheat also contains, in addition to 56 to 65 per cent. of starch, 12 to 16 per cent. of gluten, the separation of the latter renders the preparation of the starch more difficult. By the fermentation process (Halle) the gluten is rendered soluble and consequently lost, so that only wheats containing little gluten are treated in this manner. The non-fermentation process, in which the gluten is recovered, is the one usually employed, more especially because no large amount of bad-smelling liquor is formed, as is the case with the other method.

In the fermentation process the wheat is cleared and steeped in water in apparatus similar to that used with barley to be malted (*see* Fig. 153, p. 163). When sufficiently soft to be squeezed between the fingers, the wheat is passed between a pair of smooth rolls which break the epidermis without crushing it too much. The mass is placed in large tanks and covered with the acid liquid from a previous fermentation, alcoholic fermentation starting in a few days and being followed by acid fermentations (lactic, butyric, acetic, &c.) with evolution of gas ; the fermentation is complete in 10 or 12 days in summer or 20 days in winter, the liquid being then clear, yellow, and covered with mould, but not

yet smelling. The acid liquid is decanted off, and the starch separated from the bran in a finely perforated drum under a current of water. The solid residue serves as cattle-food, while the starch-milk is allowed to deposit in the ordinary vats, where it is washed ; it is then conveyed to the fine sieves and inclined channels (*see under* Potato Starch). The pure starch separated in this way should, however, contain a small proportion of gluten, since, during the drying, this facilitates the formation of so-called crystals desirable in the commercial product.

The crude starch-milk can be purified more rapidly in the Fesca-Decastro centrifuge, which has a non-perforated drum. The purer starch is deposited first in a compact layer on the inner surface of the basket and the less pure starch-milk remaining is discharged automatically before it deposits its impurities, new starch-milk being introduced and treated similarly until a thick layer of moderately pure starch is obtained. The centrifuge is stopped, the water discharged from the middle, and the yellowish, superficial portion of the starch, which contains gluten, &c., removed with a sponge. The starch is then discharged, mixed with water in a vat fitted with a stirring arrangement, and the starch-cream, sometimes after a little ultramarine or indigo carmine has been added, introduced into the suction moulds.

The drying of the cakes (*see* Potato Starch) is carried out *immediately* (to avoid mould-growth), and in winter-time this is done in an oven, the temperature of which is raised from 30° to 75° ; in the summer the drying is begun in the air. When a certain stage is reached in the drying process, the cakes shrivel at the surface ; this less pure portion is removed and the cakes broken into smaller blocks, which are wrapped in paper and dried further. Under this treatment the mass gradually assumes the radiating structure.[1]

In the *non-fermentation process* the crushed wheat is treated with a stream of water, being manipulated meanwhile in the form of a paste, which is placed on perforated channels or sieves so that the whole of the starch is gradually removed and the pasty gluten left. The starch is then deposited in the ordinary manner, while the gluten is transferred to rotating cylinders with their inner surfaces covered with points, which retain the *pure* gluten [2] ; the bran is washed away with water.

According to a suggestion by Fesca, the dry ground wheat is mixed with water and the paste introduced into a centrifuge with a perforated drum, the starch being separated by a continuous current of water, while the gluten remains in the centrifuge ; the further operations are as usual. The Fesca process is very simple and more convenient than that described above. The average yields, calculated as percentages on the wheat, are as follow : first quality starch, air-dried, 54 ; gluten flour, 12 ; bran, mixed with a little gluten and starch, 19·5 ; matters dissolved in the waste water, 14.

Statistics, *see later*. Microscopical examination, *see* p. 491.

RICE STARCH. On the average, rice [3] contains 77 per cent. of starch and less gluten (4 to 5 per cent.) than wheat, but the starch is more difficult to separate (for 1 part of gluten

[1] *Wheat flour* attains its maximum whiteness 30 to 60 days after grinding and retains it until about the sixth month, after which it slowly darkens. In America various patents have been filed, during the last few years, for obtaining this maximum whiteness more rapidly by treating the flour with ozone, chlorine, bromine, sulphur dioxide, &c., but better results are obtained with nitrogen peroxide (NO_2). According to some observers, flours bleached in this way begin to darken earlier, irregular staining taking place. The process which has given the most favourable results and has been largely applied in America and recently also in Italy, is that of Wesener (Ger. Pats. 209,550 and 232,204), according to which flour is bleached instantaneously in contact with a current of air containing mere traces of nitrosyl chloride (*see* vol. i, p. 335) ; 1 kilo of the latter is sufficient to bleach 1000 quintals or even more of flour.

[2] In presence of a little water and at a moderate temperature, the *gluten* thus obtained undergoes a slight fermentation and becomes liquid ; when dried in thin layers on metal plates, this is obtained in transparent sheets, which are used as a glue in the manufacture of boots. Or the gluten is mixed with 5 per cent. of powdered salt and made into strings in presses ; the strings are dried in an oven when they become friable and readily convertible into flour, which is used in the preparation of dough and serves as a foodstuff when mixed with other products.

[3] The mean annual *production* of rice in Italy from 1870 to 1874 was 9,800,000 hectols. ; in 1907 it was 10,450.000 ; and in 1908, 9,393,000 hectols. The exports in 1905 were 11,450 tons of raw, 3414 of semi-raw, and 44,178 of prepared rice ; the respective numbers of tons were 7850, 6450, and 40,120 in 1907, and 7691, 1936, and 35,274 in 1909. A hectolitre of rice weighs 50 to 60 kilos.

Rice (*Oryza sativa*) is an annual plant belonging to the Gramineæ indigenous to Eastern India and, according to some, to Ethiopia. In Europe it is cultivated principally in Italy and also in Spain and in the south of Russia, particularly on irrigable lands. In Japan and Brazil it is grown in the moist soil of warm, rainy regions, while in America it is extensively cultivated in Florida and Southern Carolina. In rice-plantations the bottom of the plant is kept under almost stagnant water, and, on account of the miasmata, which cause malaria, the fields should be at some distance from any habitation ; the ripening of the head is brought about by the intense heat of summer. After the harvest the rice is separated from the ear by means of suitable machines (threshers), but still retains the glumes or husk, being known as *paddy rice*. This is separated from the residues by means of concentric toothed cylinders and is then sieved and placed between two light, horizontal, stone discs (or *brahmin*),

about 1 part of starch is lost). Of all the processes which have been suggested, that devised by Orlando Jones in 1840 still gives the best results. Use is generally made of waste rice (broken rice, costing 14*s*. to 24*s*. per quintal according to the season), which is softened in a large galvanised iron or iron steeping cylinder with a conical base, by means of dilute solutions of caustic soda (0·3 per cent. in winter, 0·5 per cent. in summer). Here it is left for 5 to 15 hours, being mixed every 3 to 5 hours with a vigorous air-jet ; in winter the alkali solution is heated to 20°. The duration of the steeping varies with the quality of the rice and with the season of the year ; Italian rice requires 5 to 6 hours and Rangoon rice as much as 14 hours, the soda solution being changed in the latter case after six or eight hours. After steeping, the rice can be readily crushed between the fingers. The dissolved gluten (20 to 30 grms. per litre) is separated from the alkaline liquid simply by acidification with sulphuric acid (in order to bring the gluten into such a condition that it can be filtered in a filter-press, the temperature is raised to 80° or 1 kilo of lime is added per cubic metre of the alkaline solution). In some cases the gluten is extracted with an alkaline liquid in an apparatus similar to beet-diffusors (*see* p. 451), while in others the extraction is carried out in a vacuum with agitation. The swollen and softened rice, containing a little of the alkaline solution, is then ground between horizontal millstones, a liquid paste with 22 to 26 per cent. of starchy matter being obtained ; this is pumped up into large *square* cement tanks provided with stirrers (*see* Fig. 377), where it is treated with more dilute caustic soda solution (0·2 per cent.), care being taken in summer that the temperature does not rise sufficiently to admit of fermentation. In these tanks the separation of the starch from the liquid occupies about 1½ hours after the stirring is stopped. The liquid is decanted and the residual starch mixed with a fresh quantity of 0·2 per cent. $NaOH$ solution and left for 45 minutes to settle. In some cases this washing is repeated a third and fourth time, the thin surface layer of yellow starch containing gluten, &c., being scraped off each time before adding fresh washing water ; the scrapings from the first and second settlings are ground again in the stone mill, sieved, and mixed with the other starch. After the final washing, for which water is used, the starch-milk is conveyed to other cement depositing tanks, being previously passed through oscillating, inclined silk sieves or through revolving perforated cylinders sprayed outside with water to prevent obstruction by impurities or by solid gluten (the gluten separates best with rather hard, chalky water). The deposited starch is mixed with water and centrifuged in a non-perforated drum in the manner employed for wheat starch, the yellow surface layer being removed with a sponge. Finally, it is made into a thick paste (24° Bé. or about 50 per cent. of water ; alkalinity less than 0·2 per cent.) with water and moulded under an air-pressure of two atmospheres or with a suction-pump giving a vacuum of 600 mm. (*see* Figs. 378, 379, 380) ; the starch has not a very bright appearance if made into cakes immediately it leaves the centrifuge. In this way blocks containing 40 to 50 per cent. of water are obtained, and these are subjected to a preliminary drying in an oven at 40° to 45° ; after 5 to 8 days the mass contains 30 per cent. of water and is shrivelled at the surface, owing to efflorescence of the gluten, &c. This impure, yellow portion, which may constitute 15 per cent. of the whole, is sawn off, washed, centrifuged, filter-pressed, and then either treated again or dried and sold as a lower-grade product. The remaining blocks are dried further in the air or, more commonly, after wrapping in paper, in an oven, where the temperature is raised to 25° in two days, to 28° on the third, and then slowly to 32° or 35°. In 15 to 20 days the mass contains 12 per cent. of water and is crystallised completely in long, fragile needles with irregular surfaces ; these blocks are then exposed to the air (sheltered from dust), the normal moisture-content of 15 to 18 per cent. being thus

one of which is fixed while the other revolves ; in this way the husk is removed. The husk was formerly, and to some extent is now, separated from the rice by means of vertical pestles, which fall automatically but without touching the bottom of the mortar filled with the rice ; the grains of rice are thus rubbed, one against the other, and the husk removed. The complete removal of the husk and dust is effected by means of a simple vertical mill similar to the double one used for black powder (Fig. 210) and making 30 to 40 turns per minute. The rice is finally polished in a double vertical conical apparatus, the inner cone of which is provided with brushes of vertical metal wires and revolves at the rate of 200 turns per minute. and rubs the rice against the outer perforated cone ; the polished rice is discharged at the bottom. 100 kilos of paddy rice give 77 kilos of dehusked rice, or 67 of commercial rice, or 63 of unpolished or partially polished rice, or 59 of polished rice. The residues consist of about 1·5 per cent. waste, 20 per cent. of husk, 2 5 per cent. of risin, and 8·5 per cent. of meal, which is used as fodder, and contains, on an average, 12·5 per cent. of fat, 13 per cent. of total protein, 5 per cent. of cellulose, 45 per cent. of extractives, and 8 per cent. of ash. Italy has about 140,000 hectares under rice, a hectare of good rice land yielding 60 to 70 hectols. of rice. The following prices were quoted for rice in October 1911 : Paddy rice: Ostiglia, 17*s*. 6*d*. ; Japanese, 13*s*. 6*d*. ; Burmese, 15*s*. per quintal ; Ostiglia rice, first quality, 36*s* 10*d*., third quality, 34*s*. ; Burmese, 28*s*. ; first quality Japanese, 26*s*. 6*d*.

acquired (the alkalinity is usually below 0·15 per cent.). According to Ger. Pat. 205,763, the formation of needles is accelerated by drying the moist starch rapidly, grinding and compressing in the moulds ; the cakes are then wrapped in paper and placed in the ordinary channel ovens, through which warm, *moist* air is passed. The starch may be bleached in the ordinary way with sulphur dioxide and blued with ultramarine (about 150 to 200 grms. being added per 500 litres of dense cream before introducing it into the moulds). Difficulties are often encountered in the manufacture of rice starch, owing to the readiness with which fermentation occurs, this leading to generation of gas and to trouble in the settling and clearing of the liquids ; the remedy lies in increasing the concentration of the alkali employed or in the use of sulphur dioxide.

Rice starch is employed largely for making face powder and almost exclusively for the starching of linen, a gloss being obtained in the latter case by the addition of borax (6 to 8 per cent.), finely powdered stearic acid (2 to 3 per cent.), &c.[1]

Statistics, *see later*. Microscopical examination, *see* p. 491.

MAIZE STARCH. The maize, which has an average starch-content of 62 to 65 per cent., is softened in tepid water for three or four days and ground coarsely, the germ and bran being then separated and the remaining flour treated several times with sulphurous acid. It is then sieved and the resulting starch-milk treated as usual in sedimentation tanks, the last portions of gluten being removed. The form of the granules is shown on p. 491.

SOLUBLE STARCH. This is used in large quantities as a dressing for textile fibres and as an adhesive. It is prepared by the action on starch at different temperatures of many different reagents, such as alcohol and water, caustic soda, sulphuric acid, calcium hypochlorite, gaseous chlorine, ammonium persulphate, hydrogen peroxide, formic acid, gaseous hydrogen chloride, *diamalt* (a dense diastase syrup or malt extract, known in Germany as *diastofor*), hydrofluosilicic acid (at 80°), &c.

USES, STATISTICS, AND PRICE OF STARCH. Large quantities of starch are used as a dressing in the spinning and weaving of textile fibres, in calico printing as a thickening material, in the manufacture of paper, in the preparation of adhesive paste, in the laundry and kitchen, as well as for making dextrin and glucose.

The import duty of starch in Italy is 1*s*. 7*d*. per quintal for potato starch, &c., 9*s*. 6*d*. for rice starch, and 6*s*. 5*d*. for maize and wheat starch, &c.[2]

Germany grows the most potatoes and produces and exports (along with Holland) the largest quantities of starch. In 1903 28,764,000 tons of potatoes were produced, in 1904 24,656,000, in 1905 more than 34,000,000, in 1906 about 42,000,000, and in 1908 as much as 46,000,000 tons, the average of the three years 1908–1910 being 45,500,000 tons, about 12,000,000 tons being utilised for the manufacture of starch. The annual output of dry potato starch is about 800,000 quintals and that of green starch 560,000 quintals, besides 121,000 quintals of *wheat starch*,[3] 85,000 of *maize starch*, and 250,000 of *rice starch*

[1] The accounts of a factory dealing with 25 quintals of broken rice per day are approximately as follows :

Capital : Land and buildings, £3200 ; machinery, including duty, erecting, transport, &c., £2400 ; circulating capital, £2400 ; total, £8000.

Balance Sheet. Outgoings : 7500 quintals of rice at 16*s*., £6000 ; various chemicals, £320 ; repairs, lubricants, lighting, £200 ; packing, £600 ; salaries and wages (1 manager, 1 foreman, 1 stoker-mechanic, 7 male and 8 female hands, 1 carman and horse), £880 ; coal for motive-power and heating, 5000 quintals at 2*s*. 8½*d*., £680 ; traveller and similar expenses, £400 ; accounting, advertisements, and sundry expenses, £240 ; workmen's and fire insurance and various taxes, £320 ; unforeseen expenses, £200 ; depreciation of factory (3 per cent.), £96, and of plant (10 per cent.), £240 ; bad debts, discount, damage during transit, accidents, £400 ; 5 per cent. interest on capital, £400 ; outstanding interest, rebates, &c , £80 ; *total outgoings*, £11,076.

Incomings : Starch (75 per cent. yield), 5600 quintals at 41*s*. 6*d*. (average market price in bags and cases), £11,640 , residues, 1000 quintals at 9*s* 6*d*., £480 ; *total incomings*, £12,120.

The net profit is hence £1040, which would yield a dividend of 18 per cent. on the capital outlay. The above figures may, however, vary somewhat. Thus the price of the broken rice is sometimes as much as 14*s*. 6*d*. and, in some years, even 20*s*. per quintal, while that of the starch may fall as low as 33*s*. 6*d*

[2] **Analysis of Starch** Different starches are distinguished by their microscopical appearance (*see* p. 491). The *moisture* is determined by heating 10 grms in a weighed dish for 1 hour at 40° to 50° and for 4 hours at 120° ; a good sample should contain less than 20 per cent The *acidity* is determined on 25 grms , which is mixed with 30 c.c. of water and titrated with decinormal NaOH solution, being kept shaken meanwhile ; a drop of the liquid is removed and placed on litmus paper from time to time. If 100 grms. of the starch require 5 c.c of the alkali, it is termed *feebly acid* ; if 8 c.c are required, it is described as *acid*, and if more still, as *very acid*.

The *adhesive power* of starch is determined by heating a mixture of 4 grms with 50 c c. of water over a naked Bunsen flame and boiling for a minute until it becomes transparent and begins to form froth, the flame being then removed ; if, after shaking and allowing to cool, the paste is thick and cannot be poured out, the adhesive properties are satisfactory. The *ash* of pure starches should not exceed 0·5 per cent , and in the best qualities is less than 0·2 per cent.

[3] In 1909 Germany possessed 17 factories, which treated altogether 511,497 quintals of *wheaten flour* (containing 12 to 14 per cent. of moisture), the products being 289,236 quintals of *starch meal* (£2 per quintal), 61,777 quintals of dry starch residues (25*s*. 6*d*. per quintal), 23,676 quintals of wet residues (4*s*. per quintal), and 54,069

(1909), 54,000 quintals of the last being exported. Germany contains 500 starch factories, 450 of which are connected with agricultural concerns, while the remaining 50 are large industrial undertakings. The exportation of starch from Germany has diminished during recent years, while it varies also with the potato crop. In 1890 it amounted to 514,000 quintals, in 1896 to 340,000, in 1897 to 141,500, in 1898 to 173,300, in 1899 to 339,200, in 1901 to 255,500, in 1902 to 460,000, in 1903 to 280,000, in 1904 to 175,000, in 1905 to 133,000 (94,000 to England, 13,000 to the United States, and nearly 10,000 to Italy), in 1906 to 229,000 (147,000 to England, 24,000 to Spain, 18,000 to the United States), in 1907 to 215,622, in 1908 to 66,000, and in 1909 to 129,000 quintals.

The price in Germany in 1906 varied from 8*s.* 10*d.* to 9*s.* 7*d.* for green starch (50 per cent. of water) and from 17*s.* 8*d.* to 19*s.* 2*d.* per quintal for dry starch of the first quality.

The exportation of rice starch from Germany is also decreasing: 90,000 quintals in 1898, 65,000 in 1902, 61,500 in 1906, and nearly 60,000 in 1907.

France produces about 600,000 quintals of potato starch per annum. In 1904 Holland exported 550,000 sacks of potato starch. England imported 700,000 quintals of starch (and dextrin) in 1909. In the United States 185,000 hectols. of maize per annum are treated for the manufacture of starch.

In 1910 Italy imported the following quantities of different starches: potato starch (25*s.* per quintal), 158,460 quintals; sago, arrowroot, &c. (48*s.*), 80,000; ordinary wheat starch (36*s.*), 27,250; and fine wheat starch in cases (56*s.*), 11,226 quintals. In 1909 Italy produced 1,722,000 tons of potatoes, and in 1910 about 1,540,000, only a small proportion of which was worked industrially.

DEXTRIN is found ready formed in various vegetable juices, but is always mixed with starch and sugar, while that prepared artificially from starch by the action of heat, acid, or diastase consists of a mixture of products intermediate to starch and sugar (maltose and glucose). Several dextrins of various molecular magnitudes are known (achroodextrin, amylodextrin, erythrodextrin, &c.), the best known form having the formula $C_{36}H_{62}O_{31}$ or $(C_{12}H_{20}O_{1})_{3}$, H_2O.

According to some it has a marked aldehydic character, and hence gives all the reactions of the monoses, including those with phenylhydrazine and Fehling's reagent, while others hold that the aldehydic character is feeble, and others, again, that Fehling's solution is not reduced, even on boiling. This diversity of view is explained by the great difficulty of separating chemical individuals from the mixtures containing them; in any case all the dextrins prepared commercially reduce Fehling's solution to a greater or less extent. Dextrin is not fermented directly, and diastase does not transform it entirely into fermentable sugar (maltose), 15 per cent. remaining unchanged, although this slowly becomes fermentable under the prolonged action of diastase (*see* p. 116).

Dextrin is known also by various commercial names (*vegetable gum, starch gum, artificial gum, gommeline, British gum,* &c.), and forms a light powder having a slight smell of new bread; it is white, yellowish, or even brownish, according to the purity, the method of preparation, and the purpose for which it is intended. It is sometimes sold in semi-transparent, yellowish lumps. It dissolves completely in water when pure and has a high rotatory power ($[\alpha]_D$ = about 194°); it is insoluble in alcohol. With iodine solution it gives a reddish coloration, and boiling dilute hydrochloric or sulphuric acid converts it into glucose, while malt transforms it into maltose; with concentrated nitric acid it gives oxalic acid. Commercial dextrins often contain a little starch and glucose, so that they then give a violet coloration with iodine and reduce Fehling's solution in the hot; the specific rotation varies from 125° to 225°.

quintals of gluten (72*s.* per quintal), besides a certain amount of liquid waste for cattle-food; the total yield of starch was calculated at 71·6 per cent. Germany exported 54,740 quintals of *rice starch* in 1908 and 53,497 in 1909.

Manufacture. According to the ordinary Heuse process, 1000 kilos of starch are moistened with 2 kilos of nitric acid of 40° Bé. diluted with 300 litres of water, the paste being made into loaves which are dried in the air, ground finely, and heated for about 2 hours at 100° to 120°. For this purpose the starch is either spread in thin layers on a number of trays, which are arranged in a suitable oven, or placed in a circular Uhland apparatus (Fig. 381), the base of which is heated with superheated steam while the mass is mixed continually by means of a stirrer fitted with a number of pegs. If the temperature is raised to 130° to 140°, the duration of heating is shortened, but yellow and not white dextrin is obtained.

Dextrinification is complete when the product is entirely soluble in water and gives no longer a blue, but only a reddish brown colour with iodine solution.

The preparation of dextrin by torrefying starch is, however, a very simple process, which can also be carried out in the Uhland apparatus, the starch being stirred and heated at 225° to 250° by means of superheated steam until it assumes a brownish yellow colour and gives the reactions just mentioned. The steam-pipes are utilised for the circulation of cold water immediately dextrinification is complete.

To distinguish commercial dextrins from gum arabic, the aqueous solution is treated with either oxalic acid or ferric chloride in the cold or concentrated nitric acid in the hot: dextrin is not altered in this way but the gum becomes turbid or gelatinises. Further, dextrins are strongly dextrorotatory, while gums are almost always lævo-rotatory.

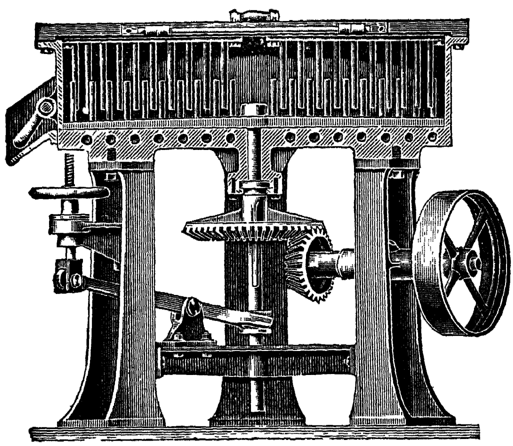


Fig. 381.

Germany produces about 190,000 quintals of different dextrins per annum, the exports being as follows: 111,525 quintals in 1901, 140,478 in 1902, 140,722 in 1903, 121,275 in 1904, 93,781 in 1905, 88,000 in 1906, 93,000 in 1907, 39,000 in 1908, 61,000 in 1909. The price in Germany varies between 24*s.* and 32*s.* per quintal. In Italy, where this industry has developed during recent years, the import duty is 6*s.* 5*d.* per quintal.

England exported 3112 tons of British gum in 1909 and 2321 tons (£67,998) in 1910.

GUMS. These are also polyoses $(C_6H_{10}O_5)_x$, which are frequently formed in plants and are soluble in water or swell up, giving viscous, sticky liquids; they are insoluble in alcohol and other solvents of the resins. **Gum Arabic** is excreted, from December to May, as an adhesive juice from the bark or, better, from the roots of certain African acacias, 3 to 5 metres in height; after drying, it has the sp. gr. 1·487, and the various components yield d-glucose and arabinose on hydrolysis. In Egypt these acacias occupy entire forests, especially in the provinces of Kordofan and Gedda (White Nile). The natives make a number of incisions in the roots, and the liquid which issues condenses in the air into nutlike masses, these being detached before the commencement of the rainy season. The grains have the colour of amber and become white when exposed to the air, so that there are two qualities of the gum. It is used in large quantities by pastrycooks and in textile dyeing and printing, and generally as an adhesive.

A similar type of gum, obtained in abundance from Senegal, issues from certain wounds of cherry- and peach-trees, while **Gum Tragacanth** is extracted from certain varieties of *Astragalus* in Servia, Syria, Persia, &c., and, after being rendered mucilaginous by prolonged contact with water, is used as a thickening material in calico printing, &c. The exports of gum tragacanth from Persia were 27,561 quintals in 1903, 30,413 in 1904, 38,937 in 1906, and 23,740 in 1908; on the Italian market the price varies from £10 to £12 per quintal.

Germany imported 58,000 and exported 23,000 quintals of gum arabic, gum tragacanth, and Senegal gum in 1905. Italy imported 10,300 quintals in 1901 and 24,070 (worth £139,000) in 1910, in which year the exports were 2345 quintals.

England imported 8300 tons of kauri gum in 1909, and 7800 tons (£637,600) in 1910, besides 10,737 tons (£176,066) of gum arabic.

The value of a gum is ascertained by determining the viscosity of its solution (*see* p. 79).

The price of gum arabic varies from £2 to £6 per quintal.

GLYCOGEN or **Animal Starch** is also a polyose $(C_6H_{10}O_5)_n$, found principally in the blood and liver of mammals. It is a white amorphous powder insoluble in cold water, and is coloured reddish violet by iodine solution. It is converted into maltose by an enzyme, whilst on the death of the animal containing it or on boiling with dilute acids it is transformed into d-glucose.

CELLULOSE, $(C_6H_{10}O_5)_n$

The actual molecular magnitude of cellulose has not yet been established but is certainly very great.[1] Like starch, it may be regarded as a multiple of $C_6H_{10}O_5$, but, while starch is able to undergo transformations (into dextrin, maltose, &c.) in the vegetable organism, cellulose represents a stable complex. Together with *lignin*, cellulose forms the principal component of the cell-walls of plants. It occurs, for instance, in wood and cotton, in different degrees of purity, while in different vegetable organisms the cells assume distinct and characteristic forms, readily recognisable under the microscope (*see* Part III, Textile Fibres). Cotton-wool and Swedish filter-paper consist of cellulose in an almost chemically pure state.[2]

Pure cellulose forms a white amorphous mass, and can be obtained by treating cotton (flocks) successively with hot dilute caustic potash, hot dilute hydrochloric acid, alcohol and ether, and drying at 125° to eliminate the water with which a small part of the cellulose is hydrolysed.

Cellulose does not dissolve in ordinary solvents, but is completely soluble in concentrated zinc chloride solution, concentrated sulphuric acid, hydrofluoric acid, phosphoric acid, xanthic acid $(C_2H_5O \cdot CS \cdot SH)$ or, best of all, in an ammoniacal solution of copper oxide (Schweitzer's reagent, prepared by dissolving freshly precipitated, well-washed copper hydroxide in concentrated ammonia solution in the proportion of CuO to $4NH_3 + 4H_2O$); from this solution it is reprecipitated as gelatinous *hydrocellulose* by acids, alkali salts, or sugar solutions. Hydrocellulose dissolves in a mixture of caustic soda and carbon disulphide, and is reprecipitated in a gelatinous state by salts, &c. These jellies are used for the manufacture of artificial silk.

Dubosc (1906) found that solutions of thiocyanates constitute good solvents for cellulose; ammonium thiocyanate, for example, gives viscous solutions from which water separates gelatinous cellulose. In dissolving in any solvent. however, cellulose generally dissociates into simpler molecular complexes, which cannot be converted into the *original cellulose* but give hydro- or oxy-cellulose.

[1] In order to determine at least *minimum* values for the molecular magnitudes of the polyoses, Skraup (1905) applied to these compounds a reaction given by the bioses; when the latter are treated with acetic anhydride and dry hydrogen chloride gas, they give chloracetyl-derivatives without undergoing hydrolysis. and the chlorine-contents of these derivatives indicate the molecular weights. In this manner the molecular weight of cellulose is found to be at least 5508, that of soluble *starch* 7440, and that of *glycogen* 16,350.

[2] From the crude cellulose or woody parts of plants, J. König (1906) separated four components giving the following reactions: (1) *hemicellulose*, which is hydrolysed by dilute mineral acids; (2) *cutin* or *suberin*, which is soluble in alkali but insoluble in ammoniacal copper oxide solution; (3) *lignin*, which is oxidisable by weak oxidising agents; (4) *true cellulose*, insoluble in dilute acid or alkali, soluble in ammoniacal copper oxide, not oxidisable by hydrogen peroxide.

The part of the cellulose which enters into the formation of the cell, but gives glucose on hydrolysis, constitutes the hemicellulose group; the hemicelluloses of lupins, certain lichens, &c., give galactose, xylose, mannose, &c., on hydrolysis.

Cross and Bevan divide celluloses into four groups: (1) celluloses which are hydrolysed with difficulty and contain no active carbonyl groups (aldehydic or ketonic), the characteristic type of this group being the cellulose of cotton; (2) celluloses which contain active carbonyl and, sometimes, methoxyl groups, and give furfural when hydrolysed with hydrochloric acid; such are the celluloses of wood and straw; (3) celluloses (or *hemicelluloses*) which are easily hydrolysed; (4) complex celluloses.

The furfural and methylfurfural formed by the celluloses of group (2) may be derived from the *pentoses* yielded by the pentosans of the celluloses or from the *furfuroids* which occur in abundance in vegetable organisms, and although they contain no pentosans yet give furfural (*see* pp. 429 and 430).

The prolonged action at moderate temperatures of acids, alkalis, and enzymes results in the gradual hydrolysis of cellulose, so that, while before hydrolysis only a brown colour is obtained with iodine solution, after the action of concentrated sulphuric acid a blue reaction is given; in this reaction the cellulose swells and dissolves into a kind of paste, and the action on this of water separates substances similar to starch (*amyloids*). If the hydrolysis is carried further the reactions of the dextrins may be obtained, dilution with water and boiling then resulting in the formation of monoses (hexoses and pentoses).[1] Cellulose may hence be regarded as composed of complex anhydrides of hexoses and pentoses, and recent investigations indicate that the behaviour of cellulose is best explained by regarding it as a *colloid* containing groups with acidic hydrogen ions, others with basic hydroxyl ions and some non-dissociated groups; the reactions of cellulose with both basic and acidic substances are explainable in this way.

Cellulose has alcoholic characters, the hydrogen of each of the hydroxyl groups being replaceable by an acetyl- (*see* p. 189) or nitro-group, &c. Not more than three or four hydroxyl groups correspond with each six carbon atoms; with nitric acid three nitrate groups can be introduced, while with acetic anhydride, in presence of sulphuric acid, esters (cellulose acetates) corresponding with four hydroxyl groups per C_6 are obtainable (Cross and Bevan, 1905).

According to H. Ost (1906) the ordinary methods of acetylation always yield triacetates of cellulose, but *hydrocellulose* is first formed as an intermediate product $(C_6H_{10}O_5)_6, H_2O$, and it is this which forms the plastic triacetate, $[C_6H_7O_5(COCH_3)_3]_n, H_2O$, used as artificial silk, &c.[2] If the action of sulphuric acid and acetic anhydride is carried too far, friable acetates of no industrial value are obtained, the ultimate product being a crystalline octoacetate of a biose, *cellose* or *cellobiose* $(C_6H_{10}O_5)_2, H_2O$, which can be liberated from the acetate by hydrolysing with alcoholic potash but is of no value industrially. The rotatory power of cellobiose is 33·7°, the solubility of its phenylosazone in boiling water 1 : 135, and the melting-point of its phenylosazone 198°; it is thus quite different from maltose (rotatory power, 142·5°; melting-point of phenylosazone, 206°; solubility of phenylosazone in boiling water, 1 : 75). The origin of cellulose in plants cannot be regarded as a condensation of starch; the latter is probably converted into glucose, which gives cellulose on condensation. The preparation of nitrocellulose (*pyroxyline*, guncotton, collodion-cotton) has already been described in the chapter on Explosives (p. 232).

Cellulose Formate (Blumer, Ger. Pat. 179,590) has also been prepared.

At 210° cotton begins to decompose with evolution of carbon monoxide and dioxide,

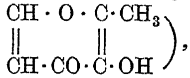
[1] Numerous attempts have been made to convert wood industrially into saccharine substances and so prepare *alcohol* (*see* p. 142), but it is only recently (1910 and 1911) that Flechsig, Ost, and Wilkening showed that cellulose can be transformed completely into fermentable glucose by dissolving it in concentrated sulphuric acid, diluting until the solution contains only 1 to 2 per cent. of acid, and then heating at 110° to 120° (but not to 125°, as was done by Simonsen, since a part of the glucose is thereby destroyed).

[2] **Cellulose Acetate** forms a horny, amorphous mass soluble in chloroform, tetrachloroethane, aniline, pure acetic acid, and boiling nitrobenzene. The less highly acetylated products are soluble in alcohol, giving a solution which, together with camphor, serves for the preparation of *cellite films* for cinematographs; these films are considerably less inflammable than those of celluloid. The triacetyl-compound is used for making artificial silk (*see later*), and is prepared by treating hydrocellulose in the cold with acetic anhydride, a few drops of concentrated sulphuric acid, and a little glacial acetic acid or phenolsulphonic acid (*see also* the following patents: Ger. Pats. 118,358, 153,350, 159,524, 163,316, 175,379, 185,837, 203,178, 203,642, 206,950, 224,330; Fr. Pats. 316,500, 319,848, 324,862, 345,764, 368,738, 368,766, 371,357, 371,447, 385,179, 385,180; U.S. Pats. 733,729, 826,229, 838,350; Eng. Pat. 9998, 1905).

More or less successful attempts have also been made to acetylate cellulose in the hot with acetyl chloride and metallic acetates, the reaction being facilitated by the addition of a small quantity of pyridine or quinoline and, in some cases, of a solvent of cellulose acetate (*e.g.* acetone, nitrobenzene, naphthalene, &c.); *see* Ger. Pats. 85,329, 86,368, 105,347, 139,669, and U.S. Pat. 709,922, according to which phenol- or naphthol-sulphonic acids are added.

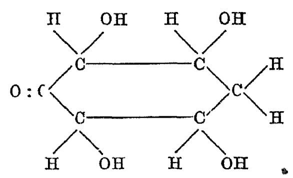
The following method of manufacture (from Fr. Pat. 347,906) admits of the direct acetylation of cotton textiles and may be taken as an example: 10 kilos of defatted cotton, containing 10 to 20 per cent. of moisture, are heated with 40 kilos of acetic anhydride (containing 0·25 per cent. of concentrated sulphuric acid) and 150 kilos of benzene, at 70° to 75°, in a reflux apparatus until a small portion of the cotton dissolves completely in chloroform; the whole mass is then pressed and dried.

Cross, Bevan, and Briggs (1907) obtain cellulose acetates easily and cheaply, without preparing hydrocellulose; cellulose is treated directly with a mixture of 100 parts of glacial acetic acid, 30 of zinc chloride, and 100 of acetic anhydride, the whole being heated for 36 hours at 45°.

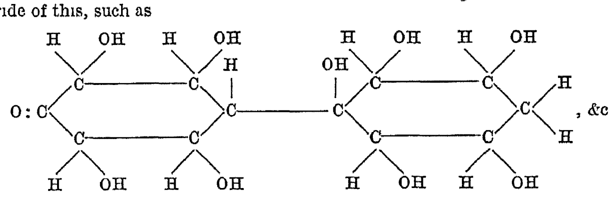
methyl alcohol, acetic acid, acetone, hydrocarbons, &c. (*see* Distillation of Wood, p. 272). By the dry distillation of pure cellulose (Swedish filter-paper) under ordinary pressure, E. Erdmann and C. Schaefer (1910) obtained about 5 per cent. of tar, 42 per cent. of acid liquors, and a residue of carbon, together with gas containing 66 per cent. CO, 19 per cent. CH_4, 11·5 per cent. H_2, &c.; from the acid liquors, acetone, formaldehyde, furfural, methoxyfurfural, *maltol* ($C_6H_6O_3$, which, according to Peratoner and Tamburello, has the constitution ), and γ-valerolactone were separated. With lapse of time or under the action of bacteria, &c., cellulose undergoes various changes (*see* Peat, Lignite, Coal, vol. i; and Methane, p. 32 of this volume).

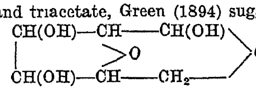
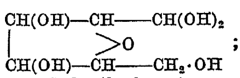
The action of sulphuric acid on cellulose varies somewhat with the concentration of the acid, the duration of the reaction, and the temperature. The concentrated acid has a gelatinising action and dissolves part of the cellulose, which is reprecipitable by water or ammonia. If the action is protracted, the very friable **Hydrocellulose**, $C_{12}H_{22}O_{11}$ [$(C_6H_{10}O_5)_2$, H_2O], is formed, but, in general, hydrocelluloses of diminishing molecular weight and increasing friability (*e.g.* cellobiose; *see above*) are successively formed. The hydrocellulose formed in the preparation of artificial silk is only slightly friable, and has probably the formula $(C_6H_{10}O_5)_6$, H_2O. Since also these hydrocelluloses exhibit rather different behaviour towards dyes, it has been suggested that the name *hydrocellulose* be given to that resulting from advanced hydrolysis by non-oxidising acids; the increase of weight during this change, owing to the addition of hydrolytic water, is 3·5 to 5 per cent., this being lost at above 125°, whilst the hygroscopic moisture is expelled at 104°. This hydrocellulose reduces Fehling's solution (Ost; Cross and Bevan, 1909). On the other hand the name *cellulose hydrate* or *hydracellulose* is given to that obtained by gentle alkaline hydrolysis, which produces an augmentation in weight of 8 to 10 per cent.; here, too, this hydrolytic water is given up at temperatures above 125°. Hydracellulose does not reduce Fehling's solution. Schwalbe (1907) measured the reducing power of hydrocellulose towards Fehling's solution.[1]

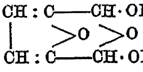
[1] Cross and Bevan proposed for cellulose the formula:



some polymeride of this, such as



On the basis of the formation of the trinitrate and triacetate, Green (1894) suggested for *cellulose* a formula (or some multiple of it) containing 3 OH, namely:  O, and for *hydrocellulose* the formula  ; these constitutions explain the formation of furfural by the decomposition of cellulose and also the formation, under the action of oxidising and bleaching agents, of *oxycellulose* containing ketonic groups which react with phenylhydrazine, reduce Fehling's solution, and admit of direct dyeing by basic dyes (*e g.* methylene blue). Two oxycelluloses are, however, distinguished: the one very similar to hydrocellulose and insoluble in boiling dilute alkali, and the other possessed of considerable reducing power and soluble in alkali.

The hardening of cellulose in the formation of wood is due to its partial transformation into LIGNIN, which is not yet well defined chemically but certainly contains methoxy-groups, which explain the formation of methyl alcohol and acetic acid when wood is distilled. According to Green, lignin is formed by dehydration of cellulose and would be a polymeride of  : But Klason is of the opinion that lignin is a kind of glucoside

When sheets of pure, unsized paper are immersed for a few minutes in sulphuric acid of 50° to 60° Bé. and then washed immediately in a plentiful supply of water, they are converted into *parchment paper* (*artificial parchment*), amyloids being formed at the surface. These artificial parchments are distinguished from the natural ones by the presence of nitrogen in the latter, and from *paraffined paper* by the extraction of the paraffin from these by ether. Parchment paper is rendered softer and more transparent by immersion in glycerine or glucose solution. If cellulose pulp is well ground and beaten in the Hollander until it forms an almost gelatinous pulp, a translucent paper can be obtained which is similar to artificial parchment and, under the name of *pergamin*, is largely used as a wrapping for foods and fatty materials; this may easily be distinguished from vegetable parchment, which is composed of cellulose hydrate (amyloids) and is hence coloured blue by a solution of iodine in potassium iodide, whilst pergamin gives no such coloration.

With concentrated zinc chloride solution, cellulose gives compounds similar to those it forms with sulphuric acid: papers thus prepared and then superposed and compressed form the so-called *vulcanised paper*; this is very hard, impermeable to water, and a bad conductor of electricity, and is used for making plaques, tubes, and noiseless gearing.

When cellulose is treated for a long time with energetic oxidising agents, it is converted into *oxycellulose* $(C_{18}H_{26}O_{16})_x$, which lowers the resistance of the tissues and, unlike cellulose, reduces Fehling's solution and fixes, although feebly, basic dyes and alizarine without a mordant. *Hydrocellulose* reduces Fehling's solution slightly and is not coloured by basic dyes.

When cellulose (spun or woven cotton) is treated in the cold with concentrated caustic soda solution (25° to 35° Bé.), it swells and becomes semi-transparent owing to the formation of *sodiocellulose*, and treatment of this with a large amount of water converts it into *hydrocellulose* (*see above*), the original appearance of the cellulose being retained. But in the hot sodiocellulose cannot be obtained (*see* Part III, Textile Fibres and Mercerised Cotton), prolongation of the action then resulting in decomposition into oxalic acid. Hygroscopic water held by cellulose is eliminated by heating at 100° to 105°; the water of hydration in hydrocellulose is determined by heating in toluene or petroleum or at 130°. The hydration occurring during mercerisation increases the weight of the cotton by 8 to 10 per cent.

Mercerised Cotton is distinguished from ordinary cotton by Knecht's test: the material is dyed in the hot with 5 c.c. of benzopurpurin 4B solution (0·1 grm. in 100 c.c. of water), and when it has taken the colour well, about 2 c.c. of concentrated hydrochloric acid are added drop by drop to the bath; the non-mercerised cotton then turns bluish black, while the mercerised remains red. If *oxycellulose* (which is formed even by the action of calcium hypochlorite) is present, the material is dyed with Congo red and the acid then added, the ordinary cotton and the oxycellulose assuming the bluish black colour, while the mercerised cotton remains red; but if the material is thoroughly washed, the pure cotton becomes red, the oxycellulose retaining its bluish black and the mercerised cotton its red colour.

PAPER INDUSTRY

As prime material in the paper industry, use has been and is still made of all the cellulosic fibres obtained from most widely differing plants,[1] linen and cotton rags, straw, wood, hemp, &c.

with two aromatic nuclei containing methoxy- and hydroxy-groups, also lateral groups, $\cdot CH : CH$ and $CH_2 \cdot OH$, besides the fundamental cellulose grouping; it is probably represented by the formula $(C_{40}H_{42}O_{11})_n$.

Dry wood contains 26 to 30 per cent. of lignin. Schultze, Tollens, and König hold the view that the hard part of wood is formed of cellulose, together with small proportions of pentosans and of lignin. The formation of wood in plants has been recently attributed by Wislicenus to the colloidal character of the plant fluids which, in the initial phase. transport into the tissues the cellulose-hydrogel as a superficial, chemically indifferent substance; in a second phase, the latter is lignified by absorption and surface gelatinisation of the colloidal metabolic substances contained in the sap. Lignocellulose is hydrolysed and dissolved by zinc chloride solution and by ammoniacal copper oxide solution, dilute acids and alkalis also exerting a hydrolysing action. Lignin gives a number of colour reactions, *e.g* with aniline sulphate (yellow), with phloroglucinol and hydrochloric acid (red); with potassium ferricyanide it forms potassium ferrocyanide, and with fuchsine decolorised by sulphur dioxide it gives a red colour; it fixes various aniline dyes (*e g.* methylene blue, eosin, &c.) directly. Wood is regarded by Cross and Bevan as an ester of lignocellulose, derived from cellulose (polyhydric alcohol) and *lignic acid* (lignin).

When pure cellulose is subjected to dry distillation, it does not yield methyl alcohol, which is, however, formed from wood; the alcohol must hence be derived from the lignin. But acetic acid is formed from both lignin and cellulose.

[1] **History of the Paper Industry** The origin of paper dates back to the second century B.C., when the first traces of it were evident in China. In early times races marked their records and writings on stone, wood,

It is not possible here to review all the wonderful mechanical improvements which rendered paper-making one of the most interesting and important industries of the nineteenth century. From the arrival of the wood in the factory to the despatch of the rolls or reams of paper, all the operations are carried out mechanically by means of perfected machinery, which is not only more rapid in its action but more accurate than hand labour.

A description cannot be given here of all the varied and ingenious dressings employed to obtain different kinds of paper, or of the mineral *loading* of kaolin, barium sulphate, gypsum, &c., with which some papers are so impregnated that the mineral substances exceed the vegetable matter, to the delight of the tradesman who sells gypsum for cheese or sausages.

What will be attempted here will be simply a brief description of the various treatments to which the raw material is subjected to convert it into paper.

Paper factories require a plentiful supply of pure water, which must not contain iron and should be filtered if turbid.

The rags, gathered in places of all sorts and in all conditions, are acquired from the rag-merchants, who separate those of wool and silk, which go to wool factories, &c., and often sort the remaining linen and cotton rags into light and dark sorts.

It is calculated that Italy produces about 600,000 quintals of rags, only some 35,000 of which are made into paper, while in 1905 20,700 quintals of vegetable rags (at 9*s.* 6*d.* per quintal) were imported, together with 30,000 quintals of animal rags (at 48*s.*) and

and parchment. In the seventh and eighth centuries the Japanese and other neighbouring peoples learnt how to prepare paper from the bark of various trees, this industry then becoming known to the Arabs, but only much later in Europe In 1190 paper made its appearance in Germany, in 1250 in France, in 1275 in Italy, and in 1430 in Switzerland.

In the East, besides bark, cotton and linen rags were also employed for paper making. In Italy the first important factory furnished with grinders and pistons for the preparation of the raw material was erected at Fabriano in 1320. With the subsequent discovery of printing, the paper industry underwent an unforeseen and marked development, and grew to enormous proportions in the nineteenth century.

About the middle of the eighteenth century, the pistons and grindstones in use up to that time for treating the raw materials were gradually replaced by the so-called hollanders, which led to an increase in the output and an improvement in the quality of the product. The demand for paper increased largely at the end of the eighteenth century, the form being improved and the price lowered.

Mechanics and chemistry came to the aid of the paper manufacturer, and as early as the beginning of the nineteenth century the paste of cotton or linen fibres. mixed in large tanks, was transformed into a thin sheet of paper by means of a revolving, perforated drum, through which the water escaped. It was about 1825 that rudimentary *continuous machines* were first employed, these supplying an uninterrupted strip of paper a metre in width at a rate of 10 metres per minute. The imposing and complex, but very accurate, continuous machines of the present day give paper as much as 4 metres wide at 150 metres per minute.

Great advances were also made in the chemical treatment of the raw materials. In the first quarter of the nineteenth century, the putrefaction to which the rags were subjected so that they might be more easily disintegrated was replaced by heating with soda and lime in open boilers and, later on, in closed boilers under steam pressure. Then came bleaching of the fibres with gaseous chlorine and subsequently with chloride of lime. The yellow cellulose obtained from straw can also be bleached in this way, and since 1830 has been used in large quantities for the commoner papers and for mixing with rags. Sizing of paper by means of resin soap, although suggested in 1800, only later came into general use.

With the rapidly increasing consumption of paper, there came a time of dearth of raw materials; cotton and linen rags were no longer obtainable in sufficient quantities, and straw could not be used alone. It hence became necessary to look for other sources of cellulose, and it is to Keller that we owe the happy solution of this pressing problem. In 1843 he succeeded in utilising wood-cellulose by means of machines which, rotating rapidly against logs of wood kept wet, gradually converted the wood into an aqueous pulp made up of the separate fibres; these machines were improved later by Volter, and the first factories of *mechanical wood-pulp* were erected. This inexhaustible material can be purified by boiling it with caustic soda in digesters under pressure and bleaching the resultant brown mass with chloride of lime; this procedure gives *chemical wood-pulp*, which to-day forms the basis of almost all kinds of paper, from the finest to the commonest

In 1884 Dahl effected considerable economy in the manufacture of wood pulp by replacing the expensive caustic soda to a large extent by sodium sulphate; calcination of the evaporated residue of the exhausted lye yields mainly caustic soda, sodium carbonate, sulphide, thiosulphate, &c., and a solution of this product acts on wood, giving a whiter and more resistant product. But although this process was applicable with advantage to straw cellulose, which gives good results only when treated with alkali or sulphate (the consumption of straw is limited nowadays by its increasingly high price), it was not convenient for dealing with the enormous quantities of wood necessary to meet the growing demands for paper. As early as 1865, Tilgman in America had attempted the chemical purification of mechanical wood-pulp by digestion with acid sulphites, and in 1874 Ekman's large factory at Bergvik was working regularly with magnesium bisulphite. Meanwhile, Professor Mitscherlich of Monaco (1872) had suggested the improvement of this process by using calcium bisulphite in large digesters under pressure. From that time and especially after the improvements introduced by Keller, the use of bisulphite spread gradually in Germany and other European countries and received a fresh impetus on the lapse of Mitscherlich's patents. At the present time, with rare exceptions—these including the treatment of straw, which contains silicates not attacked by bisulphite—almost all wood-pulp is transformed into cellulose by the bisulphite process. This process not only effects economy in the digestion of the wood-pulp, but results in an increased yield of a whiter and more resistant product.

With improvements in the chemical methods and especially by the use of energetic bleaching processes (chlorine, chloride of lime, electrolytic alkali, hypochlorite, &c.), it became possible to utilise the wood of many different trees—from the fir to the poplar—so that there is now no danger that raw material for paper-making may some day fail. In Canada alone there are still forests large enough to supply the whole world with paper for 800 years, even with a much larger annual consumption than at present.

11,200 of mixed rags (at 8*s*. 10*d*.) ; in 1910 the corresponding amounts were 15,300, 21,000, and 21,400 quintals respectively. The exports in 1905 were 15,000 (at 28*s*.) 12,000, and 210 quintals respectively ; in 1906 2631 quintals were exported, in 1908 only 508, and in 1910 less than 200 quintals. Also 65,000 quintals of macerated paper (recovered waste paper) are utilised every year in Italy.

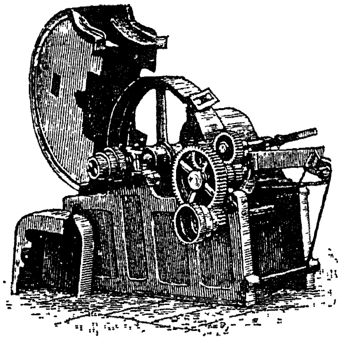


FIG. 382.

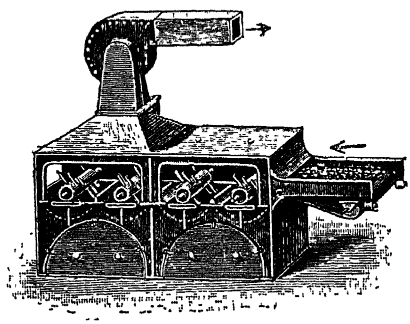


FIG. 383.

In 1909 17,777 tons of linen and cotton rags, of the value of £180,000, were imported into England.

The rags arrive at the paper factory in large bundles, some light and others dark. Preference is given to linen rags, since these give longer and tougher fibres and are used also to improve those of cotton. The first operation to which the rags should be subjected is disinfection, either by heat (great care being then taken to avoid fires) or by gaseous disinfectants (*e.g.* by introducing the bales into large iron cylinders, which are then evacuated and filled with formaldehyde vapour). In many factories, however, this disinfection is omitted, the health of the sorters being thus jeopardised. *Sorting* is carried out by workpeople who spread the loose rags on tables and separate carefully those which are more or less white and those which are coloured to varying degrees ; the larger pieces are then cut by special cutters (Fig. 382), having a number of horizontal knives fixed to the periphery of a cylinder, the seams, buttons, hooks, &c., being previously removed. The different qualities then pass to suitable machines to be cleaned and brushed. Fig. 383 shows a simple form of *duster*, in which the rags are beaten vigorously by pegs or rapidly revolving horizontal wooden cylinders and carried to the opposite end of the machine, while the dust is removed by an air-draught to be deposited in chambers or in large bag-filters of various types (Fichter, Beeth, &c.).

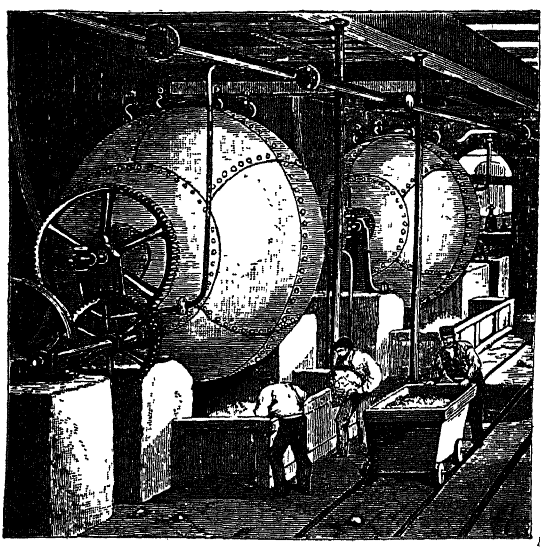


FIG. 384.

After this the rags are washed a little with water in vessels similar to hollanders (*see* p. 513) without knives but with a vaned wheel and a gauze drum for renewing the water. They are next removed to revolving spherical *boilers*, where the residual dirt is eliminated and any dye, fat, resin, starch, gum, or other impurity destroyed. This is effected by boiling, sometimes with soda or caustic soda, but more commonly with lime (2 to 5 per cent. on the weight of the rags) and water. These boilers (Fig. 384) hold as much as 2000

kilos of rags and make about two revolutions per minute, while steam is passed in through a tube traversing the axis until a pressure of 2 to 3 atmos. is reached.. The boilers are coated with insulating material, and the boiling lasts for 6 to 12 hours, according to the nature of the material. When the boiling is finished, the steam under pressure is released into the adjacent boiler, in which the operation is just starting, and the rags removed, rinsed well in water, and reduced to a fine pulp in machines similar to hollanders (*see later*) with cast-iron or reinforced concrete tanks, the knives of the drum not being set too close to those of the fixed plate. About 20 horse-power is required by the hollanders for a charge of 200 kilos of rags. The loss in weight in all the operations up to the present stage varies, according to the quality of the material, from 12 per cent. to 40 per cent. In hollanders or similar vessels holding up to 800 kilos of rags, the bleaching is carried out with a clear solution of chloride of lime, of which 2 to 10 kilos are required per 100 kilos of rags ; a little sulphuric acid (100 to 200 grms. per 10 kilos of chloride of lime) is finally added to liberate all the chlorine from the bleaching agent. In some factories fresh electrolytic solutions of sodium hypochlorite (*see* vol. i, p. 457) are used. The bleaching must not be too prolonged, and the pulp is afterwards washed in large quantities of water until all smell of chlorine has disappeared and potassium iodide starch paper is no longer turned blue or blue litmus paper reddened ; as a precaution, 30 to 50 grms. of sodium thiosulphate (antichlor) and soda are added to each vessel. The bleached mass or *half-stuff*, as it is called, is freed from water and allowed to drain for some days in brickwork chambers with pavements of absorbent grooved bricks. From these it is taken in the moist state as required for mixing with bleached wood-pulp. The mixture is beaten in true hollanders, the knives being set more or less close according as more or less fine *refined pulp* is required.

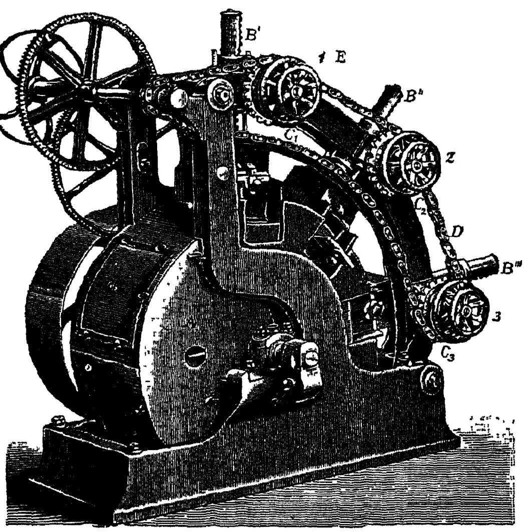


FIG. 385.

WOOD-PULP (Mechanical Pulp). The treatment to which the woody parts of the various plants suitable for paper-making [fir, pine, larch, poplar (*Populus nigra* or, better, *Populus canadensis*), beech, birch, esparto (of which Algeria exports half a million quintals annually), straw, hemp, broom, &c.], varies somewhat, as the cellulose and the surrounding lignin are present in different proportions and in different states of aggregation.[1] Logs containing few knots are cut into the required lengths (40 cm.), which, after the knots have been removed by a boring machine, are barked in another machine. The logs are then defibred by being pressed against a stone mill, which revolves rapidly and removes the fibres tangentially. This mill is about $1\frac{1}{2}$ metre in diameter and 35 to 40 cm. thick, and it revolves either horizontally or vertically (at 150 to 180 turns per minute). To the latter type belongs the *vertical grinder* devised by Voith and subsequently improved in various ways (Fig. 385). The three chambers corresponding with the three toothed rods, *B*, contain

[1] In the disintegrated wood, the proportion of *cellulose* is determined by digesting several times with sodium bisulphite solution and then treating repeatedly with chlorine at 0°, by which means almost all the constituents except the cellulose are dissolved. For the determination of the *crude cellulose* in plants, Weender's older method, modified by Henneberg and Stohmann, has been largely replaced by that of Gabriel (or Lange and König): 2 grms. of the finely divided substance are heated in a beaker with 60 c.c. of alkaline glycerine (33 grms. of caustic soda dissolved in a litre of glycerine) at 180°, the mass being then cooled to 140° and poured into a basin containing 200 c.c. of boiling water, with which it is mixed and allowed to settle. The supernatant liquid is drawn off through a siphon covered with cloth at the end dipping into the liquid, and the deposit boiled with 200 c.c. of water which is siphoned off as before. The boiling is repeated with 200 c.c. of water containing 5 c.c. of concentrated hydrochloric acid, and the residue finally brought on to a tared filter, washed with water, alcohol, and ether successively, dried and weighed as crude cellulose

To determine the *pure cellulose*, almost free from pentosans, ash, &c., König's method is used: 3 grms. of

the logs cut to the proper length, and, while the grinder revolves, these are pressed against it by the corresponding covers which are forced down by the toothed rods ; the latter connect with gearing worked by a chain, *D*, the velocity of which is proportioned to that of the grinder. The pressure is nowadays exerted hydraulically ; Fig. 386 shows a series of such vertical grinders in which hydraulic pressure is employed. Horizontal grinders (Fig.

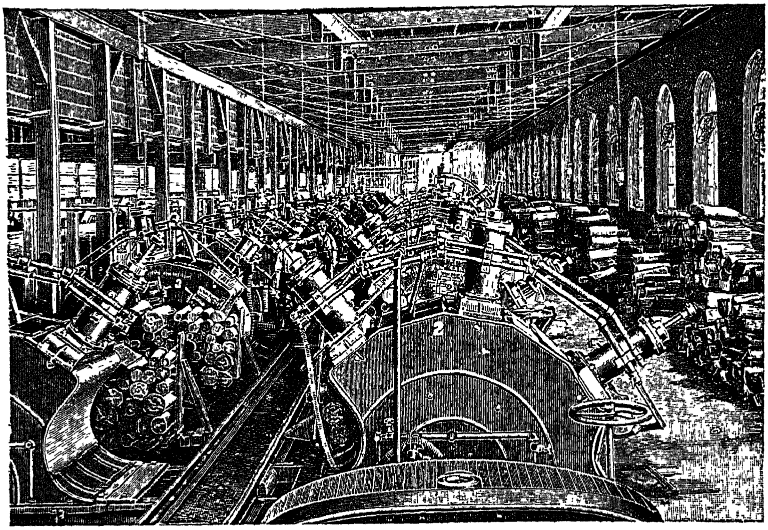


FIG. 386.

387, vertical section ; Fig. 388, general view) with hydraulic pressure are now widely used, as they admit of a larger number of logs being ground at the same time. While in operation, the grinder is continually sprayed with water to prevent heating and to remove the woody fibres as they are liberated.

According to the pressure of the logs on the grinder and to the speed of the latter

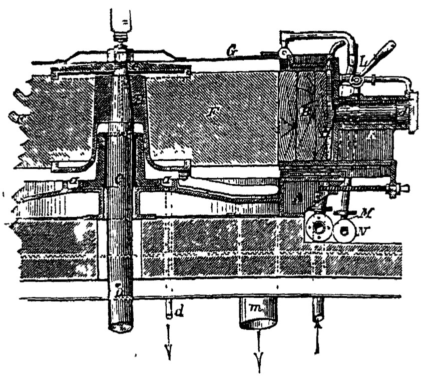


FIG. 387.

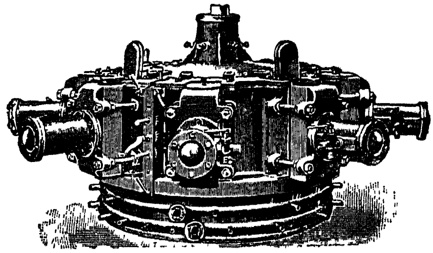


FIG 388.

a more or less fine pulp is obtained with a smaller or larger content of splinters, dust, and other irregular and unusable portions ; these are removed by means of sloping sieves,

the finely divided, air-dried material are treated with 200 c.c. of glycerine (sp. gr. 1 230) containing 4 grms of concentrated sulphuric acid in a dish which is heated in an oven at 137° for exactly one hour, the liquid being then allowed to cool to 80° to 100°, mixed with 200 to 250 c.c. of hot water, boiled and filtered hot through an asbestos filter with the help of a pump. The filter is then washed with 300 to 400 c c. of hot water, then with boiling alcohol, and finally with a hot mixture of alcohol and ether. The filter and its contents are next introduced into a platinum crucible, which is dried at 105° to 110° and weighed. The crude cellulose is then ashed by heating to redness, the loss in weight thus produced representing the crude cellulose free from ash. If, in a second estimation, the cellulose is not dried and ashed, but is repeatedly treated for several hours with strong hydrogen peroxide and ammonia, and finally washed, dried, weighed, ashed, and again weighed, the proportion of pure, white cellulose is obtained. The difference between the crude and the pure cellulose represents the *lignin*.

B and C (Fig. 389), on to which the channel, A, conveys the water to carry away the crude wood-pulp, while powerful water-jets carry the splinters (b), the good fibre (c), and the dust (E) to various collecting channels. Cylindrical or superposed sieves are also used. When the wood-pulp is to be used immediately for making paper, it is mixed with the necessary quantities of rag-pulp and dressing and worked up as described below. But generally the wood-pulp is placed on the market, in which case the water is removed and the pulp converted into sheets by sucking it on to drums of metal gauze or travelling planes, through which the water is drawn by suction; the continuous layer of pulp is cut into lengths and is best dispatched in the wet state (with 40 to 60 per cent. of water). But sometimes the sheets are dried on hot drums, although this renders difficult the subsequent treatment necessary to transform them into pulp in the hollanders.

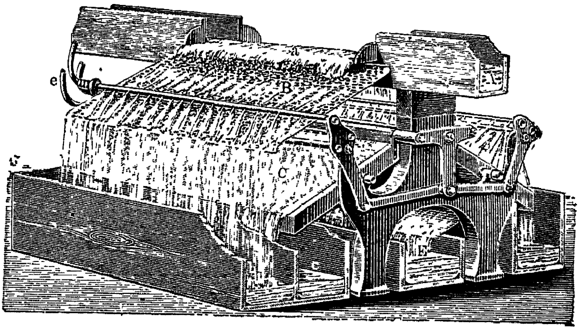


FIG. 389.

Wood-pulp is yellowish or rather brown, and still contains all the encrusting substance (lignin); it cannot be used as it is for paper, the action of light altering its colour immediately. It cannot be bleached with chloride of lime or alkaline reagents, which intensify its yellow colour; but good results are obtained with sulphur dioxide, which does not, indeed, remove the yellow tint but prevents the browning or reddening which gradually sets in.

Barked and cleaned logs yield about one-half their weight of dry wood-pulp (containing 12 to 15 per cent. of moisture).

CHEMICAL WOOD-PULP. This is obtained by removing the encrusting matter from the wood by means of various chemical agents. It was Payen who first, in 1840, attempted this purification with nitric acid, and who afterwards tried caustic alkalis, sulphurous acid, &c. The preparation of the cellulose in the chemical way can be effected by (a) the *soda process* or (b) the *bisulphite process*.

(a) The logs freed from bark and knots are converted into sticks 1 cm. thick, which are heated for some hours with caustic soda of 12° Bé. under a pressure of 6 to 8 atmos. (160° to 170°) in large digesters, 100 to 200 cu. metres in capacity. Various types of digester are in use, Fig. 390 showing the vertical type devised by Sinclair. This consists of an iron cylinder, A, 5 to 6 metres in height, with conical extremities, a charging orifice, C, a wide horizontal discharge tube, C_1, a tube, b, by which the caustic soda is introduced, and an inner perforated jacket, which is filled to the extent of four-fifths with the sticks. The reservoir, G, contains a supply of caustic soda solution, and circulation in the digester can be effected with the help of a Körting injector, the cocks of the tubes, h_1, and h, being opened; the latter conveys the alkali on to the sticks, while that collected between the perforated jacket and the inner wall of the digester ascends through h_1. The hot gases from the hearth, K, heat the digester and pass through E to the chimney. At the end of the operation the highly coloured alkali is discharged from the tap, V, and can be used for several successive treatments, being reinforced each time with a little sodium carbonate

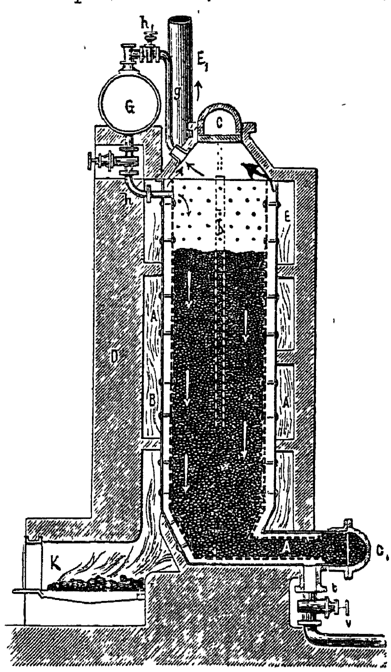


FIG. 390.

The soda is eventually recovered from this liquor by evaporating in a vacuum, calcining the residue, extracting the sodium carbonate thus formed with water, boiling with milk of lime, and decanting the resultant caustic soda solution (*see* vol. i, p. 441). But for this recovery of the soda, this process would be inapplicable. A method which is more economical and more generally used consists in reinforcing the alkali liquor first used with sodium sulphate, instead of the carbonate, for subsequent operations; the liquor is then ultimately evaporated in a vacuum and calcined, the sodium sulphate, in presence of carbonised organic matter, being converted partly into caustic soda and partly into sodium sulphide (which exerts on wood the same action as caustic soda), just as in the preparation of soda by the Leblanc process (*see* vol. i, p. 468). Extraction of the calcined mass with water yields a liquor containing sodium sulphate, sulphide, and carbonate, and is ready to act on fresh quantities of wood in the digester. Cellulose thus prepared is termed *sulphate pulp*. The concentration of the alkaline liquor is accompanied by the production of pungent and disagreeable odours, which are a source of annoyance to the neighbourhood, so that in certain countries (*e.g.* Scandinavia) such concentration is prohibited. It has been suggested to destroy these odours (due to mercaptan) by nitrous vapours.

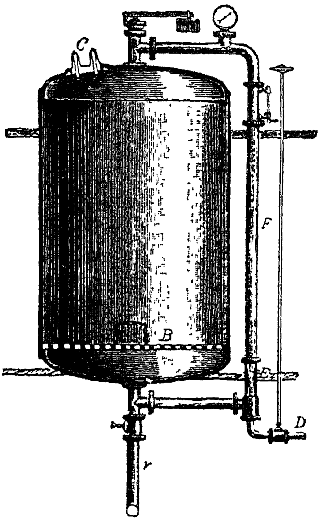


FIG. 391.

Use is also made of horizontal autoclaves arranged in series like sugar diffusors (*see* p. 451), while ordinary vertical iron digesters, as shown in Fig. 391, are largely employed. The digesters can be heated with indirect steam for 24 to 48 hours, or, more economically and rapidly, by direct steam (10 to 15 hours) to 140° to 150° (12 to 15 atmos.), but the yield is then rather lower and the mass slightly more attacked. The residual cellulose is washed, in the digesters themselves or in hollanders, with water and steam and is then mixed with the quantity of rag half-stuff necessary for the kind of paper required, the whole being then worked in the hollander into the refined pulp (*see later*).

(*b*) *Calcium Bisulphite* (Mitscherlich) or *Magnesium Bisulphite* (Ekman) *Process*. This process is the one most largely used at the present time, as it gives a cellulose of better quality than the preceding method. The wood is heated under pressure (115° to 130° or 2·5 to 4 atmos.) in large autoclaves lined inside with cement or brickwork with a solution of calcium bisulphite, $Ca(SO_3H)_2$, or magnesium bisulphite, which dissolves the encrusting matter but does not act on the cellulose [1]; the liquid is circulated inside the boiler by means of an injector or by leaving a small upper tap slightly open. The bisulphite solution of 4° to 5° Bé. (about 30 grms. of SO_2 per litre, approximately one-third being combined with lime) is prepared in very tall wooden towers (that of Harpf being as much as 55 metres high), usually lined with lead and filled with limestone or dolomite (Fig. 392). A current of sulphur dioxide ascends from the bottom to the top of the tower, while the trough, b_1, supplied by the reservoir, S, at the top, yields a fine spray of water; the bisulphite solution is collected at the bottom.

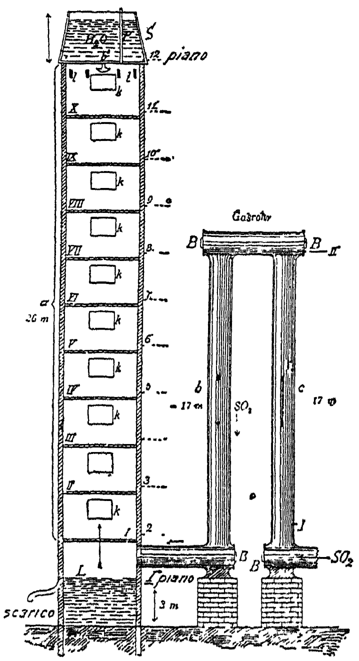


FIG 392.

[1] *Lignin* is dissolved with remarkable ease by calcium bisulphite, giving a stable soluble compound, the sulphur dioxide in which is neither detectable by iodine, nor capable of being set free by sulphuric acid, nor able to exert reducing action. Sulphurous acid alone does not act so well as the bisulphite, the lime being necessary for the formation of these sulphonic salts and for the neutralisation of the sulphuric acid always formed.

Harpf's tower has ten gratings (I to X), connected by steps not shown in the figure ; each of these can be charged and attended to independently of the others by means of the door, *k*. The first six gratings are cleaned every four weeks, but the others far less often.

The sulphur dioxide issues from pyrites furnaces into the iron tube, *c*, and passes down the earthenware pipe *b*, *B B* being for convenience of cleaning. The calcium or magnesium bisulphite solution deposits its suspended matter in *L* and is then discharged into storage tanks. When the whole of the tower is to be washed, the plug, *P*, of the cistern is raised.

To ascertain the completion of the action of the bisulphite on the wood in the digesters, a sample of the liquid is removed now and then and treated in a graduated tube with ammonia ; when the calcium sulphite occupies one-sixteenth of the volume of the sample the heating is stopped, and when this fraction is reduced to one thirty-second the operation is finished and the coloured liquor can be discharged. The wood is sometimes treated with steam before being introduced into the bisulphite boiler. The whole operation, including charging and discharging, preliminary treatment of the wood and action of the bisulphite, lasts 50 to 60 hours. The spent bisulphite liquor is highly coloured and charged with salts, gummy matters, tannin, glucose, pentoses, acetic acid, nitrogenous compounds, &c., and it is usually forbidden to turn it into watercourses or bottomless wells ; so that it is often purified by precipitation of the sulphite with lime, the calcium sulphite being then reconverted into the bisulphite by sulphur dioxide. Attempts have also been made, but with little success, to evaporate the residual liquor and so obtain adhesive gummy substances utilisable in the preparation of coal briquettes. In a factory with two boilers, each of 120 cu. metres capacity (12 to 15 metres high, 3·5 to 4 metres in diameter, and about 2 cm. thick), each of these is charged with about 200 quintals of wood and 85 cu. metres of bisulphite solution. With a monthly output of 1000 quintals of cellulose, the daily production of spent liquor is 30 cu. metres, the organic residue amounting to 8 per cent. and the ash to 2 per cent. The rational disposal of these spent liquors is always a serious problem, which still awaits solution ; the attempts made to prepare alcohol from them are mentioned in the note on p. 142.

The gases emitted can be deodorised by means of nitrous vapours, which attack the mercaptans.

The yield of cellulose varies with the quality of the wood, but is about 50 to 55 per cent.

(*c*) *Electric Process.* This was proposed by Kellner, and consists in passing through closed receptacles containing the wood a solution of sodium chloride at 126°, through which an electric current passes ; the chlorine, hypochlorous acid, and caustic soda act together in the nascent state, dissolving the encrusting substances of the wood and liberating the cellulose. This process has not yet been much used.

MECHANICAL REFINING OF THE CELLULOSE AND MECHANICAL WOOD-PULP. The mass of wood, more or less finely divided, extracted from the digesters is coarsely defibred in suitable disintegrating machines, and the cellulose and the mechanical pulp, either together or separately, according to the kind of paper required, are introduced into the so-called hollanders, where they are completely defibred and converted into a very fine pulp ; bleaching with calcium hypochlorite and the subsequent washing are also carried out in the hollanders, as is the addition of dressing, colour, size, resin, alum, &c., necessary for the desired paper.

The hollander beating machine consists of a large, oblong wooden or, better, cement vessel (*A*, Figs. 393 and 394), in the middle of which is a vertical, longitudinal partition, *B*, which does not extend to the ends of the vessel. In one part of the vessel is a large revolving drum, *D*, furnished at its periphery with a number of cutters which circulate the water containing the cellulose or mechanical pulp. The bottom of this part of the vessel is in the form of a ridge (*PR*, Fig. 394), and at a point, *F*, on one of the slopes are fitted cutters ; the drum can be moved up or down by means of the lever, *HG*, and the distance between its cutters and those at *F* thus adjusted as required. The movement of the water produced by the rotation of the drum causes almost the whole of the cellulose and pulp to pass between the fixed and revolving cutters, and after some time the woody fibres swim separately in the water. As the process goes on, the knives are gradually brought closer together until the desired degree of fineness is attained. The mass passes up the plane, *P*, down the plane, *R*, round the partition, *B*, again up the plane, *P*, and so on.

The washing water can be changed by immersing in the free half of the vessel a fine gauze drum from which the water can be aspirated by means of a pump. This drum is then raised by the chain and pulley, *R* (Fig. 393), and fresh water introduced into the vessel. To avoid spurting from the drum, *D*, it is fitted with a cover, *T*. In the base of the vessel and in front of the inclined plane is a recess for catching pieces of iron or stone accidentally present in the wood-pulp, the cutters thus being protected from damage. Fig. 193 on p. 237 shows a battery of hollanders, which are also used for guncotton.

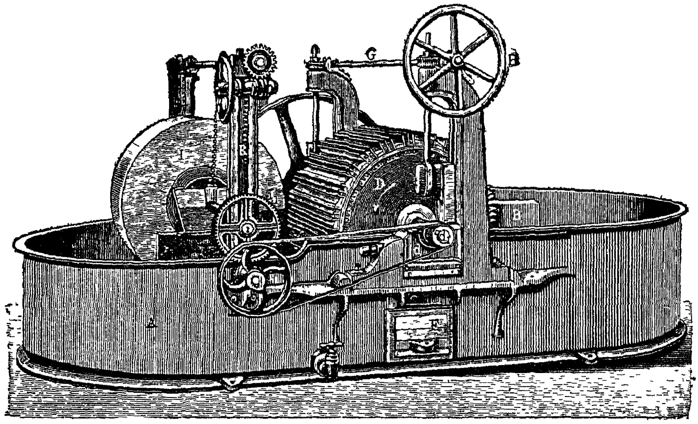


FIG. 393.

SIZING AND FORMATION OF THE PAPER. The refined pulp in the hollander, containing the different raw materials (rags, wood-pulp, cellulose, &c.) in the requisite proportions, is blued and sized before being transferred to the continuous machines. The blueing is effected by adding, a short time before the end of the beating, 500 to 1000 grms. of ultramarine, Prussian blue, or aniline blue ; a little later the size is added, which renders the paper impervious to water and prevents ink from running on it ; if blotting-paper or filter-paper is required, the sizing is omitted. Sizing can be carried out on the finished

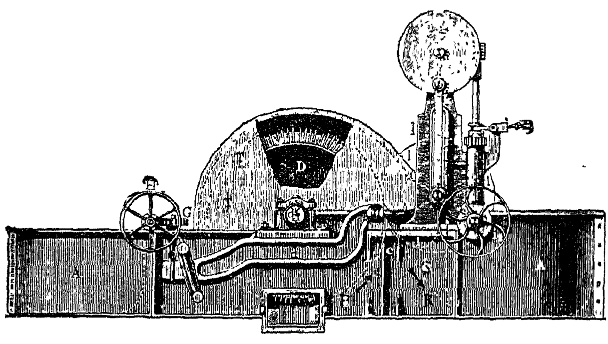


FIG. 394.

paper, but it is usually preferred to add the dressing directly to the finished pulp while this is still suspended in water, since in this way all the fibres become coated with the size without losing the power of adhering, one to the other, to form a homogeneous, felted mass of paper. Animal size was at one time used, but, owing to its ready putrefaction or alteration even while it is being applied, it has been almost entirely replaced by resin (colophony) previously rendered soluble (resin soap) by means of caustic soda. With water this soap forms very fine, homogeneous and persistent emulsions, the efficacy of which may be increased by the addition of starch paste (in amount sometimes equal to that of the resin) or of casein dissolved in dilute soda solution. The total dressing added amounts to 2 to 5 per cent. of the dry paper.

In order to precipitate the resin in a fine state of division on the fibres, a solution of aluminium sulphate (or of potash alum) is added to the homogeneous mixture of pulp and resin soap; as was shown by Wurster, this effects the precipitation of the resin, starch (or casein), and a very small amount of aluminium resinate. Nowadays one-half of the aluminium sulphate is sometimes replaced by the cheaper magnesium sulphate. The so-called *loaded papers* are obtained by adding, in addition, a considerable quantity (sometimes 50 per cent.) of kaolin, barium sulphate, talc, or calcium sulphate.

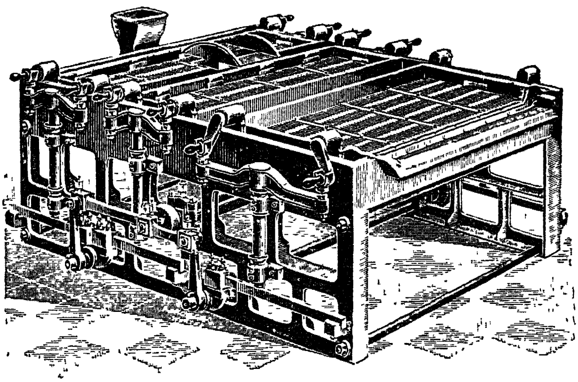


FIG 395.

The colouring-matters (mineral dyes, lakes, or substantive aniline dyes) are also added directly to the finished pulp, organic dyes being the more commonly used. The lakes are produced by mixing basic dyes with the pulp and then precipitating with tannin solutions; for direct dyeing, substantive dyes (*see later*, Colouring-Matters) are employed. Powdered lakes obtained by precipitating either acid aniline dyes with aluminium hydroxide or basic dyes with tannin or tartar emetic may also be used.

After all these additions have been made, separation of any of the components from the homogeneous pulp is prevented by conveying the latter into two vats, where it is kept in motion by stirrers, the resultant milk being more or less dense according to the thickness of paper required. Before going to the continuous machine to be converted into paper, the pulp is passed through a purifier (Fig. 395) which removes any clots of fibre still present. This purifier consists of two or three slightly inclined, oscillating plates, perforated with very fine slots; when the pulp is fed regularly on to these plates, the fine fibres pass through while the lumps are discharged into channels provided for the purpose.

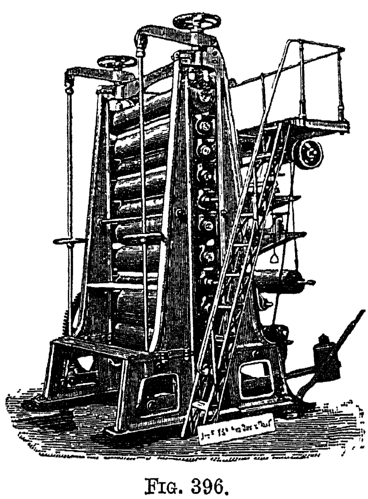


FIG. 396.

The homogeneous pulp collected under the vibrating plates is conveyed to the continuous machine at an almost absolutely regular speed, and on this depends the uniformity in the thickness of the resultant paper; the pulp regulator or feeder should hence be constructed with great care. If this homogeneous pulp is placed on a very fine sieve, the water passes through, leaving a thin layer of interlaced, adhering fibres which can be removed in the form of a wet sheet. The preparation of the paper in the continuous machine takes place in a similar manner. The pulp is distributed uniformly on a very fine endless copper gauze after a good proportion of its water has been removed by draining and suction. A cloth then passes the wet sheet to a pair of rolls, which compress it and give it more consistency; other rolls heated to 130° gradually dry the paper, while others, again, press it and give it a little polish. When it leaves the endless gauze, the paper is sufficiently consistent to be conveyed to the supercalendar (Fig. 396), where it is pressed and polished between several pairs of rolls. Other machines wind it into rolls, cut it, rule it, &c.

A large modern continuous machine may cost several thousands of pounds. A general view of such a machine is shown in Fig. 397; the two vats of pulp are seen at *a*, while *b* represents the circular feeder carrying buckets, *c* the drum sieve which collects the pulp and passes it as a wet sheet to the metal gauze, *d*, this transferring it to the cloth at *f* and

passing back round the rollers, *e*, underneath to take up fresh pulp; *g* shows the drying rolls and *h* where the cloth returns, the continuous length of paper being drawn off at *i* to the winding apparatus.

It is not possible here to consider the different kinds of paper now manufactured, or the different pulps required, or the special modern machines devised to meet all the requirements of the trade, but a few words may be devoted to the testing of paper,[1] the pulp used being recognisable under the microscope by the magnitude and form of the fibres (*see* Figs. 398 *et seq.*). As will be shown in the chapter on Textile Fibres, the fibres of paper are corroded and somewhat distorted and resemble the original fibres only in certain characters.

The fibres of the white fir are shown in Fig. 398 at *A* and in transverse section at *B*; they are brown and are characterised by the pores arranged in concentric circles. Fig. 399 shows at *B* altered cotton fibres and at *L* those of linen. Fig. 400 gives an idea of the microscopical appearance of mechanical wood-pulp of the conifers (fir, pine, &c.) with medullary rays, while Fig. 401 shows chemical pulp from the conifers; in the latter case, the concentric circular pores are less marked and the fibres more homogeneous. Fig. 402 shows straw cellulose with the very thin parenchymatous cells, *a*, rounded at the ends, and the superficial toothed cells of the epidermis, *o*, mixed with the bulk of ordinary elongated and striated fibres. *Esparto* fibres resemble those of straw to some extent but

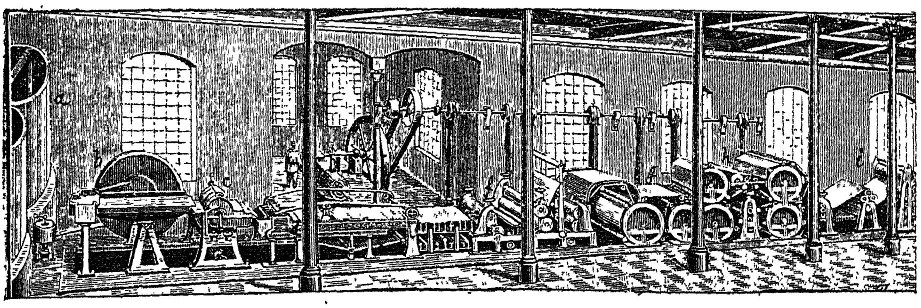


FIG. 397.

are lacking in thin and terminal cells, while the toothed edges are different in nature and are found in smaller cells than in straw; esparto contains certain isolated fibres having

[1] Testing of Paper. The presence of *mineral loading* is detected by determining, in a platinum crucible, the *ash* of 1 to 2 grms. of the paper, cut up and dried at 100° to 105°; non-loaded paper contains 0·4 to 2·5 per cent. of ash. To detect the presence of mechanical wood-pulp, the paper is immersed in an aqueous solution of aniline sulphate, which imparts a golden-yellow colour to the crude wood fibre; or use may be made of aqueous phloroglucinol faintly acidified with hydrochloric acid, this dyeing the crude wood fibre (mechanical pulp) red. The *impermeability* or *solidity of the sizing* is determined by Leonardi's method; on to the paper, stretched and inclined at 60°, a solution containing 1 per cent. of ferric chloride, 1 per cent. of gum arabic, and 0·2 per cent. of phenol is allowed to fall drop by drop so as to form a number of moist strips which are then allowed to dry; similar strips, crossing the first and perpendicular to them, are next made with a solution containing 1 per cent. of tannin and 0·2 per cent of phenol; the formation of a black stain of tannate of iron at the point of intersection indicates bad sizing, absence of stain shows perfect sizing, and stains more or less grey denote more or less good sizing.

Resin sizing is recognised by pouring a few drops of ether on to the paper and allowing them to evaporate; the formation of transparent rings indicates the probable presence of resin. Or a few grms. of the paper may be boiled with absolute alcohol containing a few drops of pure acetic acid, the solution being afterwards poured into distilled water; if the latter becomes turbid, the presence of resin is certain.

To detect *animal sizing*, a few grms of the paper are boiled with a very small quantity of distilled water, the liquid being filtered, highly concentrated and treated with a solution of tannin; if size is present, whitish grey flocks are formed, which, when observed under the microscope in contact with a dilute solution of iodine in potassium iodide, are seen to be coloured brown, while if starch is present this is coloured blue; the test for starch may be made directly on the paper itself.

The presence of *free mineral acid* is ascertained by boiling the paper in a little distilled water and noting if the solution turns Congo-red paper blue or black.

For the *microscopical examination* (*see* Figs 398–402), the fibres are liberated as follows: 3 to 5 sq. cm. of the paper are boiled and vigorously shaken for two minutes with 3 to 4 per cent. caustic soda solution, the pulp thus formed being poured on to a very fine metal sieve and washed well with tepid water. The fibres are then tested microchemically with solutions containing (1) 6 parts of iodine, potassium iodide, 10 parts of glycerol, and 90 of water, and (2) 100 parts zinc chloride, 10·5 of potassium iodide, 0·5 of iodine, and 75 of water, the clear liquid being, in this case, decanted from the precipitate formed; linen, hemp, and cotton are coloured pale to dark brown by solution (1), the thin fibres remaining almost colourless, while with solution (2) a more or less intense wine-red coloration is obtained.

An alcoholic solution of phloroglucinol containing hydrochloric acid does not colour pure cellulose but reddens

the form of teeth or elongated pears. Spain exported more than 90,000 tons of esparto in 1872 and about 46,000 in 1900. Algeria now exports 80,000 tons, Tunis 30,000, Tripoli 75,000, and Morocco 4000. Algeria contains 5,000,000 hectares under esparto. England imports about 200,000 tons of esparto per annum.

STATISTICS. Books and reviews often contain contradictory and fantastic statistics concerning the output of paper. According to the most trustworthy data, the world's production of paper and pasteboard in 1906 amounted to about 8,000,000 tons, and that of *cellulose* in 1908 was estimated at 1,600,000 tons of the value of £16,000,000.

In 1904 the United States produced 2,000,000 tons of mechanical pulp and 4,000,000 tons of paper and pasteboard, worth £32,000,000 ; in 1860 the output was 200,000 tons, of the value of £5,200,000. The wood converted into mechanical pulp represented a value of

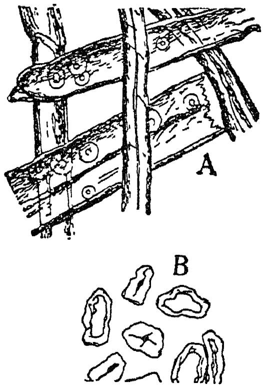


FIG. 398

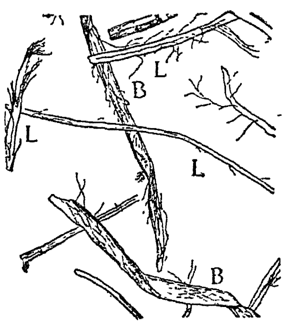


FIG. 399

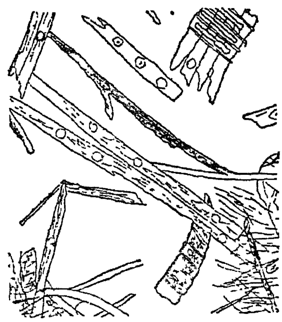


FIG. 400.

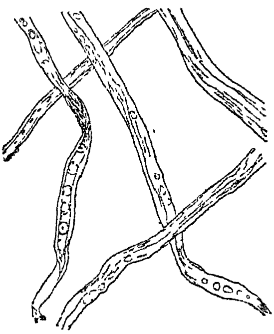


FIG. 401.

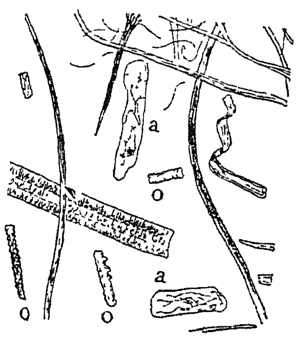


FIG. 402.

£5,600,000 in 1908, and more than £6,800,000 (from 253 factories) in 1909. The value of the exports was £1,480,000 in 1904 but is rapidly increasing, and already exceeds £4,000,000; in 1904 there were 1200 paper and mechanical pulp factories, with a total capital of about £40,000,000, one-half of th s representing machinery.

In 1911 the United States imported 263,000 tons of mechanical wood-pulp, 213,000 tons of cellulose (£1,296,000), and 86,000 tons of bleached pulp (£737,800).

impure cellulose, the presence of wood-pulp (*i e.* impure cellulose) in paper being hence detectable in this manner. Further, aniline sulphate or naphthylamine hydrochloride colours impure cellulose yellow, but does not alter pure cellulose.

The *bursting strain* of paper, called also the *degree of elasticity*, is determined in the directions of the length and breadth by means of suitable dynamometric apparatus, the elongation which occurs before rupture being expressed as a percentage of the length (this varies from 1 5 to 4 per cent. for different papers). The *breaking length* expresses the length of a uniform strip of paper which would tear under its own weight if suspended from one end : if a strip 10 cm. wide of paper of which 1 sq. metre weighs 70 grms breaks under a load of 3500 grms. the breaking length is $\frac{3500}{70 \times 10} \times 1000 = 5000$.

The *resistance to folding* is determined roughly by crushing and rubbing an irregular ball of the paper between the hands; when different papers are compared in this way, that with the least number of creases is the best.

Germany in 1899 contained 900 paper and pasteboard factories, 72 wood-cellulose factories, 30 straw-cellulose factories, and 600 mechanical wood-pulp factories, using a total of 125,000 hydraulic horse-power and 75,000 steam horse-power, employing 65,000 operatives, and producing 270,000 tons of cellulose (550,000 tons in 1909), 300,000 tons of mechanical pulp, and 800,000 tons of paper and pasteboard. In 1884 the output of paper and paste-board was 200,000, and in 1904 more than 1,200,000 tons of the value of £12,600,000. The imports in 1904 were 24,000 tons of paper and pasteboard, the same quantity of mechanical pulp, and about 47,000 tons (32,550 tons in 1909) of cellulose; the exports were 64,000 tons of cellulose in 1904 (147,088 tons in 1909), 6000 tons of mechanical pulp, and 250,000 tons of paper and pasteboard. In 1908 Germany imported 833,480 tons of wood for paper, and in 1909 about 1,653,000 tons, exporting about 40,000 tons.

The price of wood-cellulose in Germany was 42*s.* per quintal in 1852 and is to-day less than 16*s.*

In Norway the first manufactory of mechanical pulp was erected in 1870 and the first of cellulose in 1880, and in 1905 the paper industry occupied 8000 workpeople, the output being 100,000 tons of paper. In recent years this industry has advanced considerably, 27 factories now possessing a total of 60 continuous machines and the production of paper in 1910 being 150,000 tons (of the value of £1,520,000), nine-tenths of this being for export.

In 1891 Sweden possessed 40 paper factories, occupying 3000 workpeople and producing 36,000 tons of paper, worth £480,000. In 1906 the output of paper was 209,000 tons (£2,400,000), and in 1907, 225,000 tons (£2,560,000). Sweden produced mechanical wood-pulp to the value of £3,080,000 in 1906 and £3,760,000 in 1907, part of it being exported.

France produced about 75,000 tons of paper in 1860, about 60,000 operatives being employed in the industry in 1901; in 1904 the output was almost 450,000 tons.

In Russia the consumption of paper is continually increasing, but the amount produced is almost stationary: 163,800 tons in 1897, 177,000 in 1900, and 205,000 (£7,600,000) in 1906; so that Russia imports a considerable quantity of paper, even from Japan and China, but more especially from Finland, whose exports of paper to Russia have increased sixfold during the last ten years.

Finland exported nearly 43,000 tons of mechanical pulp and about 13,000 tons of cellulose in 1906, largely to Russia.

Austria produced about 350,000 tons of paper in 1904.

England in 1860 produced about 100,000 tons of paper and now produces rather less than Germany; in 1909 the imports included, besides rags (*q.v.*), 197,501 tons of esparto, &c., of the value of £720,000, and 749,740 tons of mechanical wood-pulp and cellulose, worth £3,480,000.

The imports of raw materials for paper-making into England were valued at £4,741,230 and the exports at £820,730 in 1911; the imports of paper of different kinds amounted to £6,574,500 and the exports to £3,311,867 in 1911.

In 1906 Spain produced more than 35,000 tons of paper.

The paper industry in Italy has increased very considerably in recent years, the production being 60,000 tons in 1876 and almost 70,000 in 1886, the importation of *cellulose* being as follows: 1800 tons in 1886; 13,600 in 1896; 24,300 in 1901; 42,000 in 1905; 46,700 in 1907; 54,000 in 1908; and 63,100 tons, of the value of £706,400, in 1910. The production of cellulose in Italy is very small, there being but three factories. In 1896 28 *mechanical pulp* factories produced 10,000 tons of the pulp, 4200 tons of which were imported in the same year and 8741 tons (£62,936) in 1910. The total production of paper and cardboard in Italy in 1907 was about 200,000 tons; 30,000 tons of this was used for daily papers weighing 45 grms. per sq. metre (24*s.* to 28*s.* per quintal).

The *Customs duty* on paper in Italy varies from about 6*s.* to 36*s.* per quintal for different qualities.

The following numbers represent the mean annual consumption of paper in kilos per inhabitant for various countries, these being regarded as a rough indication of progress:[1]

[1] About 75,000 new books are published per annum in the whole world, these requiring 25,000 tons of mechanical pulp alone. In addition, about 30,000 periodicals are published with a total circulation of nearly 11,000,000,000 copies and for these 1000 tons of mechanical pulp are consumed per day.

Of the total output of paper, 32 per cent. is for ordinary printing, 10 per cent. consists of fine paper and writing paper, 10 per cent. of brown paper and cardboard, 6 3 per cent. of fine cellulose and rag paper for fine printing; 5 per cent. of straw paper and card, 3 per cent. of paper for placards, &c., 3 per cent. of wall-paper, 0 6 per cent.

United States, 19·3 ; England, 17·2 ; Germany, 14 ; France, 11·5 ; Austria, 9·5 ; Italy, 7·5 ; Spain, 2·5 ; Russia, 2·3 ; Servia, 0·6 ; China, 0·6 ; India, 0·13.

of drawing paper, 0 5 per cent of silk paper, cigarette paper, and paper for making flowers ; 0 4 per cent. of blotting- and filter-paper, &c.

Although the consumption of paper has increased to an extent that would have been incredible a few years ago, yet the day is far distant when a scarcity of raw material will be experienced. Canada alone, with its 322,000,000 hectares of *forest land* can supply the whole world for several centuries. Of other reserves of forest the most important are those of the United States, 200,000,000 hectares ; Russia, 184,000,000 ; Queensland, 86,000,000 ; Siberia, 38,000,000 ; British India and Burmah, 26 000,000 ; Finland, Sweden, and Japan (excluding Formosa and Hokkaido), 20,000,000 each ; Germany, 17,000,000 ; Austria and France, 10,000,000 each ; Hungary, Croatia, and Slavonia, 9,000,000 ; New Zealand, 8,000,000 ; Asiatic Turkey, 7,000,000 ; Norway, 6,000,000 ; Hokkaido (Japan), 6,000,000 ; Italy. 4,500,000, &c. In Burmah and elsewhere there are immense tracts of bamboo, which will one day be utilised for the manufacture of paper

It cannot, however, be denied that an immense amount of wood is used for building purposes, and in Italy, for instance, many of the forests have been destroyed, so that the imports of wood, which in that country amounted to £840,000 in 1871, increased to £2,000,000 in 1900, to £2,840,000 in 1905, and to still greater extents (mostly from Austria-Hungary and America) in recent years (*see* vol i, p. 204).

PART III. CYCLIC COMPOUNDS

THE aliphatic series contains various groups of closed-chain compounds (*e.g.* lactones, uric acid derivatives, anhydrides of dibasic acids), which are readily opened by simple reactions giving ordinary open-chain compounds of the fatty series.

Numerous substances are, however, known containing a closed-chain nucleus which is composed of 3, 4, 5, or more commonly 6, carbon atoms united in a special manner and is resistant to the most energetic reagents. These compounds form the important group of aromatic compounds.

Other groups of cyclic substances are also known with nuclei composed, not of carbon atoms alone, but of several elements, *e g.* pyridine, C_5H_5N, in which the nucleus contains 5 carbon atoms and 1 nitrogen atom ; pyrrole, C_4H_5N, with C_4 and N in the nucleus ; furan, C_4H_4O, with a C_4O nucleus ; thiophene, C_4H_4S, with a C_4S nucleus ; pyrazole, $C_3H_4N_2$, with the nucleus C_3N_2, &c. These compounds are called *heterocyclic*.

There are also many substances derived from more complex nuclei formed by the condensation of two or more of the nuclei mentioned above, *e.g.* naphthalene, $C_{10}H_8$, in which are condensed two benzene nuclei held together by two carbon atoms common to the two nuclei, and quinoline, with a nucleus analogous to that of naphthalene but composed of one benzene and one pyridine nucleus.

AA. ISOCYCLIC COMPOUNDS

These contain 1 or several homogeneous carbon atom rings, and can be subdivided, according to the type of linking, into (1) **Polymethylene Compounds**, which contain singly linked carbon atoms and are less resistant to chemical reagents than (2) **Benzene Derivatives**, where the carbon atoms are linked very differently (*see later*). Compounds of the first group approach those of the aliphatic group in their chemical properties and are hence intermediate to methane and benzene derivatives.

I. CYCLOPARAFFINS AND CYCLO-OLEFINES OR POLYMETHYLENE COMPOUNDS

TRIMETHYLENE (Cyclo*propane*), $CH_2<\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}$, is obtained by the action of sodium on $\alpha\gamma$-dibromopropane, $CH_2Br\cdot CH_2\cdot CH_2Br$, the bromine being eliminated and the chain closed. It is a gas which liquefies at a pressure of 5 to 6 atmos. and combines very slowly with bromine or hydriodic acid giving open-chain compounds, so that it is easily distinguished from propylene $CH_2 : CH\cdot CH_3$. Its heat of combustion is much greater than that of propylene, into which it is partially converted at 400°.

Its derivatives are obtained from ethylene bromide by means of the ethyl malonate synthesis (*see* p. 308).

Trimethylenedicarboxylic Acid, $\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}>C<\begin{matrix}CO_2H\\ \\ CO_2H\end{matrix}$, was obtained by Perkin by the interaction of ethylene bromide and ethyl sodiomalonate.

TETRAMETHYLENE (Cyclo*butane*) is not known in the free state, but derivatives of it are obtainable by syntheses similar to those used for trimethylene compounds.

PENTAMETHYLENE (Cyclo*pentane*), $\begin{array}{l} CH_2 \cdot CH_2 \\ | \\ CH_2 \cdot CH_2 \end{array} \!\!> CH_2$, is a liquid boiling at 50°; its derivatives are prepared by the ethyl malonate synthesis.

According to Baeyer's tension hypothesis (*see* p. 88 and Fig. 247, p. 306), it is easy to understand why pentamethylene is the most stable of the preceding compounds, a ring of five carbon atoms being the only one which can be formed without tension of the linkings. Indeed, while trimethylene combines with Br or HI with rupture of the ring, pentamethylene does not unite with bromine and resists the action of nitric or sulphuric acid like a saturated hydrocarbon, the properties of *saturated open-* and *closed-*chain compounds hence differing but little.

KETOPENTAMETHYLENE (Cyclo*pentanone*), C_5H_8O, is obtained by the dry distillation of calcium adipate:

$$\begin{array}{l} CH_2 \cdot CH_2 \cdot COO \\ | \\ CH_2 \quad CH_2 \cdot COO \end{array} \!\!> Ca = CaCO_3 + \begin{array}{l} CH_2 \cdot CH_2 \\ | \\ CH_2 \cdot CH_2 \end{array} \!\!> CO\,;$$

by reduction and subsequent treatment with HI it gives *pentamethylene*, whilst oxidising agents convert it into glutaric acid, these reactions proving its constitution. **Ketohexamethylene** is obtained similarly by distilling **Calcium Pimelate**, $C_7H_{10}O_4Ca$, and higher homologues by distilling the corresponding calcium salts of higher dibasic acids; **Calcium Suberate**, $C_8H_{12}O_4Ca$, for example, yields **Ketoheptamethylene** (*suberone*). The yield diminishes with increase of the number of carbon atoms.

CYCLOPENTADIENE, $\begin{array}{l} CH:CH \\ | \\ CH:CH \end{array} \!\!> CH_2$, is a liquid boiling at 41°, and is found in the first distillate of crude benzene and also in illuminating gas; it combines with iodine and with hydrogen sulphide. The presence of two double linkings in the nucleus is deduced from the fixation of four atoms of halogen. The two hydrogen atoms of the CH_2 readily react, *e.g.* with acetone, giving intensely red *hydrocarbons*:

$$\begin{array}{l} CH:CH \\ | \\ CH:CH \end{array} \!\!> CH_2 + \begin{array}{l} CH_3 \\ \\ CH_3 \end{array} \!\!> CO = H_2O + \begin{array}{l} CH:CH \\ | \\ CH:CH \end{array} \!\!> C:C \!< \begin{array}{l} CH_3 \\ \\ CH_3 \end{array};$$

this compound is known as dimethylfulvene, fulvene being an isomeride of benzene of the structure $\begin{array}{l} CH:CH \\ | \\ CH:CH \end{array} \!\!> C:CH_2$.

II. BENZENE DERIVATIVES OR AROMATIC COMPOUNDS

It was observed by several chemists about the middle of last century that a whole series of compounds, mostly aromatic in nature, besides exhibiting certain common physical and chemical characters, showed on analysis proportions of hydrogen very low in comparison with those of carbon and also very low compared with those of hydrogen in saturated or unsaturated compounds of the methane series, *e.g.* C_nH_{2n+2}, C_nH_{2n}, C_nH_{2n-2}, &c.

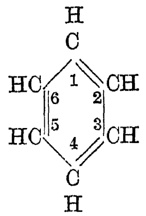
In general the hydrocarbons of these substances correspond with the fundamental formula, C_nH_{2n-6}, and the various transformations of the aromatic substances often yield **Benzene**, C_6H_6, from which they can again be prepared. If the constitutional formula of benzene were an open-chain one, it would be necessary to assume the presence of double or triple linkings between carbon and carbon which would lead to ready addition of bromine and to ready oxidation. But these reactions do not occur, and the great stability of the compounds of this group, and of benzene in particular, can be explained only by the existence of a stable nucleus of carbon atoms, probably joined in the form of a closed ring.

It was found later that benzene forms only one monosubstituted product (nitrobenzene, bromobenzene, &c.), and that all the hydrogen atoms of benzene exist under similar

conditions; three isomeric disubstituted products (*e.g.* dinitro- or dibromo-benzene) are, however, known.

With the empirical formula C_6H_6 correspond the three rational formulæ: (α) $C_4(CH_3)_2$, (β) $C_3(CH_2)_3$, and (γ) $(CH)_6$. Formulæ (α) and (β) would give only two isomeric disubstituted products, whilst in the case of (γ), if the six CH groups were joined in the form not of an open chain but of a closed ring, the six hydrogen atoms would be under the same conditions, and the formation of a single monosubstituted product and of three isomeric disubstituted products would be explained.

It was Kekulé who, in 1865, first advanced the ingenious hypothesis that the fundamental compound of aromatic substances is benzene, the constitutional formula of which must be represented as a closed, hexagonal chain of carbon atoms united alternately by single and double linkings, the fourth valency of each carbon atom being united to a hydrogen atom. Such an arrangement is figured in the scheme



or, if the six carbon atoms are represented by tetrahedra (*see* p. 18 *et seq.*), in the diagram shown in Fig. 403. The carbon atoms combined with the substituents in the three disubstituted derivatives would then be: (*a*) 1 and 2 (*ortho*-derivatives), (*b*) 1 and 3 (*meta*-derivatives), and (*c*) 1 and 4 (*para*-derivatives); the 1 : 5- and 1 : 6- compounds would be identical with the 1 : 3- and 1 : 2-compounds respectively. For the sake of shortness, the terms ortho-, meta-, and para- are contracted to o-, m- and p-, these being prefixed to the names of the compounds.

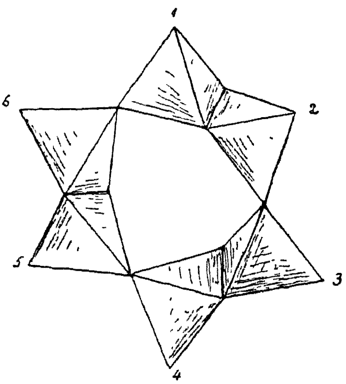


FIG. 403.

The constitutional formula given for benzene by Kekulé and also those of Claus (1867), Baeyer (1868), Körner (1869), and Ladenburg (1870) would seem to indicate the possible existence of 2 ortho-substituted derivatives, since the 1 and 2 carbon atoms are joined by a double linking and numbers 1 and 6 by a single linking. Hence Claus and Körner proposed the hexagonal formula with the fourth valencies of the carbon atoms joined diagonally (para-linking) (Fig. 404, *A*), while Ladenburg preferred the prismatic formula (Fig. 404, B_1, B_2, and B_3), and Armstrong and Baeyer the centric formula, with the fourth valencies in a latent (or potential) state and directed towards the centre (Fig. 404, *C*); *see also* Fig. 405.

In order to obtain a better interpretation of the formation of the disubstituted isomerides of benzene, Kekulé (1872) developed his theory further on the assumption that the linkings between the carbon atoms are to be regarded as vibrations, so that carbon atoms 2 and 6 of the Kekulé formula are in identical conditions. These oscillations would explain why benzene does not unite readily with halogens or ozone (*see* p. 88; *also Ann. Soc. Chim.*, Milan, 1907, p. 116, and *Berichte der deut. chem. Gesell.*, 1908, p. 2782) or give Baeyer's permanganate reaction (*see* p. 88), thus behaving almost like a saturated compound. But even Kekulé's *oscillatory formula* does not explain completely the optical and thermal behaviour of the aromatic compounds or the interesting results obtained by Baeyer on the hydrogenated derivatives of benzene subsequently to 1886. Indeed, when two or four hydrogen atoms are added to benzene so as to form dihydro- or tetrahydrobenzene, the latter are found to be quite different from true aromatic compounds and to

resemble olefine compounds ; it must, then, be assumed that where the hydrogen has not been added, true double linkings are formed capable of combining with halogens or ozone and of giving Baeyer's permanganate reaction. Baeyer's centric formula would harmonise with this behaviour, since each of the valencies directed towards the centre is kept in equilibrium with all the others, stability being thus conferred on the molecule ; if, then, two or four of the central valencies are used in the addition of hydrogen or other groups, the remaining central valencies become true, olefinic, double linkings.

There are, however, aromatic compounds, especially those with several condensed benzene nuclei, with which Baeyer's centric formula alone cannot be assumed. In 1899

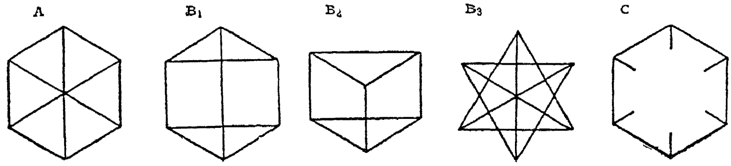


FIG. 404.

Thiele attempted to harmonise all the chemical and physical phenomena observed with benzene and its derivatives on the assumption that when two carbon atoms are united by a double linking the two affinities are not completely utilised, parts of the unsatisfied valencies (*partial valencies*) remaining. These are regarded as bringing about addition processes, and are represented by dotted lines, *e.g.* $\underset{\vdots}{C}=\underset{\vdots}{C}$, $\underset{\vdots}{C}=\underset{\vdots}{C}-\underset{\vdots}{C}=\underset{\vdots}{C}$, &c. But when, as in the latter formula, a conjugated system of double bonds is present, the addition of hydrogen, halogens, &c., occurs only at the two extreme carbon atoms, the partial valencies of the two middle atoms forming a new *inactive double bond*, $\underset{\vdots}{C}=C\underset{\smile}{-}C=\underset{\vdots}{C}$; after the addition at the extreme carbon atoms, the central inactive bond *becomes active again*, the constitution then being, $\underset{\overset{\cdot}{H}}{C}-C=C-\underset{\overset{\cdot}{H}}{C}$

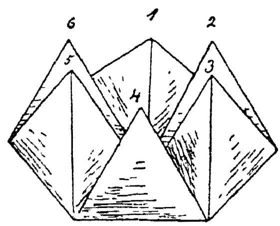
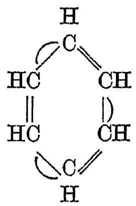


FIG. 405.

In Kekulé's benzene formula, we may assume the existence of three conjugated double bonds with three inactive bonds, thus,



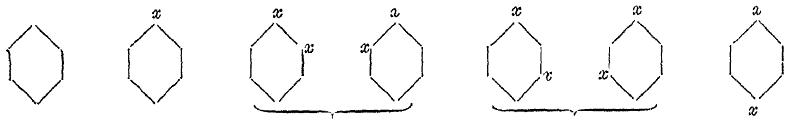
; it would then be clear why benzene, being without partial valencies, would not readily form additive products, and why, when even a single inactive double bond is broken down, true active olefinic double linkings would appear (*see* Theory of Double Linking, *Note* on p. 88).

A plausible explanation of the constitution of benzene is also arrived at by means of the ideas of *motochemistry*, according to which double or single linkings are represented by double or single vibrations or blows per unit of time (E. Molinari, *Gazzetta Chimica Italiana*, 1893, vol. ii, p. 47, and *Journal fur praktische Chemie*, 1893, p. 113).

ISOMERISM IN BENZENE DERIVATIVES

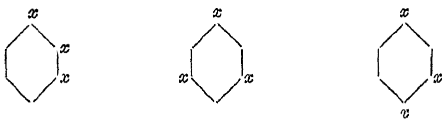
It has been seen already that when one of the hydrogen atoms of benzene is replaced by a halogen or an organic residue, the same monosubstituted compound is always obtained, no matter at what point of the molecule the substitution occurs. If two substituent groups, either similar or different, are introduced, three disubstituted derivatives are obtainable. If the benzene

molecule is represented simply by a hexagon, each angle of which indicates a carbon atom united with a hydrogen atom, replacement of the latter by another atom or group (x, y, z, &c.) may be shown by placing the symbol of the substituent at the angle of the hexagon. With disubstituted compounds, if one group is assumed to occupy the position 1, the other may go to either 2 or 6 (*ortho*-position), 3 or 5 (*meta*), or 4 (*para*).



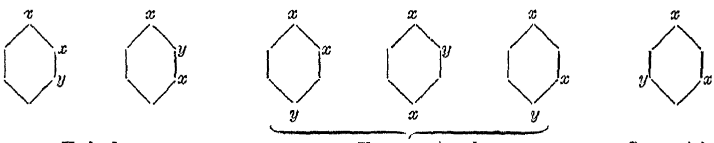
Benzene   Monosubstituted benzene   Ortho-compounds 1 : 2- and 1 : 6- (identical)   Meta-derivatives 1 : 3- and 1 : 5- (identical)   Para-derivative

With the trisubstituted derivatives, three isomerides are possible when the three substituents are similar (1 : 2 : 3- or *vicinal*, identical with 1 : 6 : 5- ; the symmetrical, 1 : 3 : 5-, identical with 2 : 4 : 6- ; and finally, the unsymmetrical, 1 : 2 : 4-, identical with 1 : 5 : 4-) :



Vicinal (*v*-)   Symmetrical (*s*-)   Unsymmetrical (*as*-)

When one of the three substituents is different from the remaining two, six isomerides are possible :



Vicinal   Unsymmetrical   Symmetrical

With four similar substituent groups, it will readily be seen that three isomerides are possible.

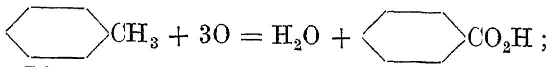
The number of isomerides may be further increased in cases where one or more of the substituents form lateral chains capable of isomerism, *e g.* saturated hydrocarbon or unsaturated alcohol or acid groups ; in these compounds, further replacement of hydrogen may occur either in the benzene nucleus or in the side-chain, fresh cases of isomerism being thus possible.

It was Körner (1869–1874) who first showed how it is possible to determine experimentally the *positions* of the various substituent groups in the benzene nucleus ; examples will be given later.

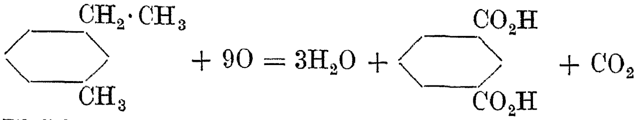
GENERAL CHARACTERS OF BENZENE DERIVATIVES

While the saturated hydrocarbons of the aliphatic series offer considerable resistance to oxidising agents and to concentrated sulphuric or nitric acid, those of the aromatic series readily give nitro-derivatives with nitric acid, and sulphonic derivatives, having an acid character, with sulphuric acid : $C_6H_6 + HNO_3 = H_2O + C_6H_5\cdot NO_2$ (nitrobenzene) ; $C_6H_6 + H_2SO_4 = H_2O + C_6H_5\cdot SO_3H$ (*benzenesulphonic acid*). In the latter, the sulphur is united directly to a carbon atom of the benzene nucleus, this being confirmed by the fact that benzenesulphonic acid is also obtained by the action of oxidising agents on thiophenol, $C_6H_5\cdot SH$, in which the sulphur is known to be joined to carbon.

Oxidation of aromatic hydrocarbons containing side-chains leads to the replacement of the latter by *carboxyl* groups, CO_2H, the benzene nucleus remaining unchanged ; in this way the various aromatic acids are obtained :



Toluene Benzoic acid



Ethyltoluene Isophthalic acid

The halogen substitution derivatives, which are readily obtained by the direct action of the halogens, have less reactive properties than the halogen compounds of the aliphatic series and are more resistant to substitution.

The hydroxyl-derivatives (*e.g.* phenol, $C_6H_5\cdot OH$) are more decidedly acid in character than the alcohols of the fatty series, the *phenyl* group, C_6H_5, for example, being more negative than the ethyl group ; their resistance to oxidising agents is similar to that of the tertiary alcohols, to which they are analogous in constitution, the group $>C\cdot OH$ being present in both cases.

The amino-derivatives, which are readily obtainable by reducing the nitro-derivatives ($C_6H_5\cdot NO_2 + 6H = 2H_2O + C_6H_5\cdot NH_2$, aniline) with intermediate formation of azo-compounds (*q v.*), are easily converted by the action of nitrous acid into diazo-compounds ; the latter are formed only seldom and with difficulty in the case of aliphatic compounds.

In their last investigations Körner and Contardi (1908) show how, with the substitution products of benzene, the formation of one isomeride rather than another sometimes depends on minimal differences in the physical conditions under which the reactions take place. Thus, in the nitration of aniline or of halogenated derivatives, a very slight difference in the concentration (even in the second decimal place of the specific gravity) is sufficient to alter the yield very considerably or even to give entirely different products.

FORMATION OF BENZENE AND ITS DERIVATIVES

When vapours of aliphatic compounds are passed through red-hot tubes, the products formed contain aromatic compounds. At a red heat acetylene gives benzene (the reverse reaction is also possible) : $3C_2H_2 = C_6H_6$.

When allylene, C_3H_4, is distilled with dilute sulphuric acid, mesitylene, $C_6H_3(CH_3)_3$ (1 : 3 : 5), is obtained, while under similar conditions crotonylene, C_4H_6, forms hexamethylbenzene, $C_6(CH_3)_6$.

In presence of concentrated sulphuric acid, several aliphatic ketones undergo condensation to aromatic hydrocarbons ; thus, acetone forms 1 : 3 : 5-trimethylbenzene, $3C_3H_6O = 3H_2O + C_6H_3(CH_3)_3$.

Acetoacetaldehyde, $CH_3\cdot CO\cdot CH_2\cdot CHO$, when liberated from its sodium derivative, is transformed immediately into triacetylbenzene, $C_6H_3(COCH_3)_3$.

Various aromatic compounds can also be obtained by the action of sodium on ethyl bromoacetoacetate or ethyl succinate, by heating ethyl sodiomalonate and by certain other syntheses.

From the tar obtained by distilling coal, wood, or lignite, many aromatic compounds can be separated : 5 to 10 per cent. of naphthalene, 1 to 1·5 per cent. of benzene and toluene, besides quinoline, anthracene, &c.

Benzoic and salicylic acids, bitter almond oil, &c., occur naturally in the vegetable-kingdom.

A. AROMATIC HYDROCARBONS

Those with saturated side-chains are colourless, refractive liquids of characteristic odour, insoluble in water, but extremely soluble in ether or absolute alcohol; they are lighter than water (0·830 to 0·806).

General Methods of Preparation. (1) Alkyl chlorides and aromatic hydrocarbons in presence of aluminium chloride give mono- and poly-substituted hydrocarbons, which can be separated by fractional distillation: $C_6H_6 + CH_3Cl = HCl + C_6H_5 \cdot CH_3$ (Friedel and Craft's synthesis); intermediate aluminium compounds are first formed. Ferric chloride, zinc chloride, or zinc turnings act in the same way as aluminium chloride. The latter salt also brings about the decomposition of the higher hydrocarbons into more simple ones.

(2) In presence of sodium, monobromo-substitution derivatives of aromatic hydrocarbons and alkyl bromide or iodide give higher aromatic hydrocarbons (Fittig's synthesis, analogous to that of Wurtz for the aliphatic series):

$$C_6H_5Br + C_2H_5I + Na_2 = NaBr + NaI + C_6H_5 \cdot C_2H_5.$$

(3) Distillation of calcium salts with soda lime (analogous to the synthesis of aliphatic hydrocarbons):

$$\underset{\text{Calcium benzoate}}{(C_6H_5CO_2)_2Ca} + Ca(OH)_2 = 2CaCO_3 + 2C_6H_6.$$

(4) Aromatic sulphonic derivatives give the hydrocarbons when heated with sulphuric or hydrochloric acid, best in presence of steam: $C_6H_5 \cdot SO_3H + H_2O = H_2SO_4 + C_6H_6$. On this reaction is based the method used for separating aromatic hydrocarbons from those of the aliphatic series, the former with concentrated sulphuric acid giving soluble and the latter (paraffins) insoluble sulphonic acids.

(5) When an aromatic hydrocarbon is dissolved in an alcohol in presence of zinc chloride at about 300°, water separates and a higher hydrocarbon is formed: $C_6H_6 + C_5H_{11}OH = H_2O + C_6H_5 \cdot C_5H_{11}$.

DISTILLATION OF TAR

The cheapest and most abundant hydrocarbons used as raw material for the preparation of large numbers of important aromatic compounds (from artificial perfumes to aniline dyes) are obtained by the distillation of tar. While at one time this product constituted an unpleasant and inconvenient residue of the illuminating gas industry (*see* pp. 36–38, 52, and 81), it is now so much in demand by large manufacturers of chemical products that it is sometimes very scarce, and attention has been turned to the utilisation of the tar produced in metallurgical coke factories, this having been formerly discarded.

Westphalian coal gives, on an average, 2·5 per cent. of tar, that of Saahr as much as 4 per cent., and that of Silesia even more than 4 per cent.

The first attempt to utilise tar dates back to 1834 when, in a works at Manchester, it was distilled out of contact with air in primitive retorts, the liquid products being collected and the residual pitch employed for making black varnish. Bethell subsequently patented a process for obtaining from tar creosote oil for the impregnation and preservation of wood.

Still later the more volatile products of the distillation of tar were used both as an illuminant and as a cleaning liquid. Nitrobenzene was then prepared from it to replace essence of mirbane.

But it became possible to develop an industry for the regular utilisation of tar only after the wonderful discovery by Perkin (1856), who prepared synthetically the first artificial coal-tar dye, thus laying the foundation of one of the most important industries for which the nineteenth century is famous.

COMMONEST AROMATIC HYDROCARBONS WITH A SINGLE BENZENE NUCLEUS

	Name	Rational formula	Position of substituents	Melting-point	Boiling-point	Specific gravity
C_6H_6	Benzene . . .	—	—	+ 5·4°	+80·4°	0·874 $\left(\frac{20°}{4°}\right)$
C_7H_8	Toluene or methylbenzene . .	$C_6H_5 \cdot CH_3$	—	liquid	110°	0·869 (16°)
C_8H_{10}	o-Xylene=o-dimethylbenzene . .	$C_6H_4(CH_3)_2$	1 : 2	− 28°	142°	0·893 (0°)
	m-Xylene=m-dimethylbenzene . .	,,	1 : 3	− 53°	139°	0·881 (0°)
	p-Xylene=p-dimethylbenzene . .	,,	1 · 4	+ 13°	138°	0·880 (0°)
	Ethylbenzene . .	C_6H_5 C_2H_5	—	liquid	136°	0·883 (0°)
C_9H_{12}	Hemimellithene = trimethylbenzene (*v*)	$C_6H_3(CH_3)_3$	1 . 2 : 3	,,	175°	—
	Pseudocumene = trimethylbenzene (*as*)	,,	1 : 2 · 4	,,	169·5°	0·895 (0°)
	Mesitylene = trimethylbenzene (*s*)	,,	1 . 3 : 5	,,	165°	0·865 (14°)
	n-Propylbenzene .	C_6H_5 C_3H_7	—	,,	159°	0·867 (14°)
	Isopropylbenzene = cumene . .	,,	—	,,	153°	0·866 (16°)
$C_{10}H_{14}$	Prehnitene = tetramethylbenzene .	$C_6H_2(CH_3)_4$	1 : 2 . 3 : 4	− 4°	204°	—
	Isodurene = tetramethylbenzene (*as*)	,,	1 . 2 : 3 : 5	liquid	195°	—
	Durene = tetramethylbenzene (*s*)	,	1 : 2 : 4 : 5	+ 80°	192°	—
	m-Cymene = methylisopropylbenzene .	$C_6H_4 \cdot CH_3(C_3H_7)$	1 : 3	liquid	175°	0·862 (20°)
	Cymene = methylisopropylbenzene .	,,	1 : 4	,,	175°	0·856 (20°)
	n-Butylbenzene . .	$C_6H_5 \cdot C_4H_9$	—	,,	180°	0·864 (15°)
	sec. Butylbenzene .	,,	—	,,	175°	0·867 (15°)
	Isobutylbenzene .	,,	—	,,	171°	0·871 (15°)
	tert Butylbenzene .	,,	—	,,	167°	0·871 (15°)
$C_{11}H_{16}$	Pentamethylbenzene .	$C_6H(CH_3)_5$	1 : 2 3 : 4 : 5	+ 51·5°	231°	0·847 (104°
	n-Amylbenzene . .	C_6H_5 C_5H_{11}	—	liquid	202°	0·860 (22°)
	Isoamylbenzene .	,,	—	,,	194°	0·885 (18°)
$C_{12}H_{18}$	Hexamethylbenzene .	$C_6(CH_3)_6$	1 : 2 : 3 : 4 : 5 : 6	+ 166°	265°	—
$C_{13}H_{20}$	n-Heptylbenzene .	C_6H_5 C_7H_{15}	—	liquid	109° (10 mm.)	—
$C_{14}H_{22}$	n-Octylbenzene . .	$C_6H_5 \cdot C_8H_{17}$	—	− 7°	263°	0·852 (14°)
$C_{16}H_{26}$	Pentaethylbenzene .	$C_6H(C_2H_5)_5$	1 : 2 : 3 . 4 : 5	liquid	277°	0·896 (20°)
$C_{18}H_{30}$	Hexaethylbenzene .	$C_6(C_2H_5)_6$	1 . 2 . 3 : 4 : 5 : 6	+ 129°	298°	0·830 (130°)
$C_{22}H_{38}$	Cetylbenzene . .	$C_6H_5 \cdot C_{16}H_{33}$	—	+ 27°	230° (15 mm.)	0·857 (27°)
$C_{24}H_{42}$	Octadecylbenzene .	C_6H_5 $C_{18}H_{37}$	—	+ 36°	249° (15 mm.)	—
	Hexapropylbenzene .	$C_6(C_3H_7)_6$	1 · 2 · 3 : 4 : 5 : 6	+ 118°	—	—
$C_{25}H_{44}$	Trimethylcetylbenzene	$C_6H_2(CH_3)_3(C_{16}H_{33})$	1 : 3 : 5 : 2	+ 40°	258° (15 mm.)	0·845 (40°)

Numerous industries then arose for the more complete and more rational utilisation of tar—for employing to the best advantage the various products of its fractional distillation. Since that time a continuous series of mechanical improvements in the plant and chemical ones in the processes have been introduced. Improvements in the coke furnaces to admit of the collection of the whole of the products of distillation and of the rational recovery of the heat have been dealt with in vol. i (p. 366).

After separation from the ammoniacal liquors of gas manufacture (by centrifugation), tar forms a dense, almost viscous, blackish (since it contains 10 to 30 per cent. of suspended carbon particles) liquid of sp. gr. 1·1 to 1·3. It contains many varied acid, basic, and indifferent products ; the first can be extracted by agitating with aqueous alkali solution, the second with acids, while the neutral compounds, consisting principally of aromatic hydrocarbons, form the residue. The composition of tar varies, however, with the nature of the coal, the type of furnace, and the temperature of distillation.

It seems that tar contains at least 300 different substances, of which 150 have been established either directly or indirectly and 90 have been isolated with certainty and studied, although only four have wide application in the pure state : benzene, phenol, toluene, and naphthalene.

Only to a small extent is tar used as it is : for varnishes, coal briquettes, bitumenised

paper, *lampblack*,[1] treating roads to render them less dusty, &c. But for such purposes the residue from the distillation of tar can also be used.

A little tar is used in preparing the basic lining of Bessemer converters for the manufacture of steel.

Nowadays, however, tar is mostly subjected to distillation for the extraction of the following products: (1) *Indifferent substances*, in which benzene hydrocarbons predominate (benzene, toluene, xylene, tri- and tetra-methylbenzene, and, to a still greater extent, naphthalene, anthracene, &c.), those of the methane series being small in amount (these occur abundantly in the distillation products of *lignite-tar*, *see* pp. 81 and 82). Small quantities of nitrogen compounds occur, such as acetonitrile, benzonitrile, carbazole and pyrrole derivatives, and also traces of carbon disulphide, thiophene, cumarone, &c.; (2) *Acid substances*, among which phenol (carbolic acid), cresol, xylenol, and the naphthols abound. (3) *Basic substances*, which are found in small amount and contain small proportions of pyridine and quinoline compounds and a trace of aniline.

Wood-tar is of less value than coal-tar; its most important constituents are those soluble in alkali, these consisting of methyl ethers of polyhydric phenols (pyrocatechol, pyrogallol and homologues, forming creosote oil), which are used for making guaiacol. *Wood-tar* is distilled in a vacuum, the gases which do not condense being utilised for power or heating purposes, as they have a calorific value of 6000 to 9000 cals. per cubic metre.

The distillation products of coal-tar are approximately as follows: benzene and its homologues, 1·5 to 2·5 per cent.; phenol and its homologues, 0·5 to 2; pyridine and quinoline bases, 0·2 to 0·3; naphthalene, 4 to 6; heavy oils, 20 to 26; anthracene and phenanthrene, 0·5 to 2; pitch, 55 to 62 (38 being asphalte soluble in benzene and 24 carbon or insoluble); ammoniacal liquor, 4; gas and loss, 1·25.

Another source of aromatic products is the distillation and heating of lignite-tar and

[1] Lampblack is prepared by the incomplete combustion of tar, colophony, vegetable oils, the pitch or heavy oils from tar, &c. The liquid or fused substance of the receivers, *a*, is passed through pipes to the long pans, *A* (Fig. 406), in which it is heated while a carefully regulated minimal air-current is passed over the surface of the

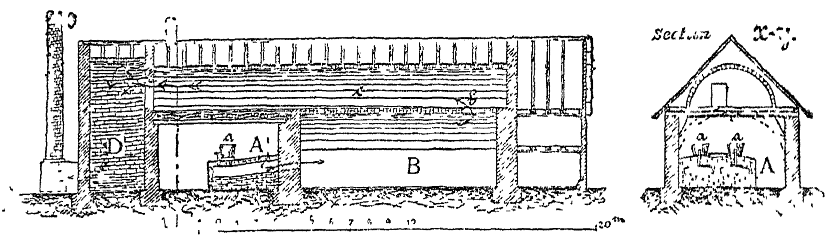


Fig. 406.

liquid so as to burn the vapours incompletely and separate the greater part of the carbon in a free and finely divided state. This is carried away by the air into the first arched chamber, *B*, where it is partly deposited, then into the second arched chamber, *c*, and finally into *D* (before the chimney, *O*), in which the final traces of lampblack are deposited on a thin cloth in front of the mouth of the shaft. This operation is continued for five days, the sixth day (Sunday) being occupied in cooling down and the seventh in restarting. A very fine lampblack is obtained by burning paraffin oil in a kind of lamp with a wide thin jet and allowing the flame to impinge on an iron cylinder inside which water circulates; the cylinder thus cools the flame and the lampblack deposited on it is removed from time to time by an automatic scraper With more or less intense cooling the lampblack has a lower or higher specific gravity. 100 kilos of tar yield 25 kilos of lampblack, while 100 kilos of resin residue give 20 kilos Lampblack contains, in addition to free carbon, tarry impurities and oily distillation products. Attempts have been made, apparently without success, to prepare lampblack by exploding acetylene with a measured proportion of air in closed vessels. The Frank process seems to be more advantageous; in this, acetylene is burned with a certain proportion of carbon monoxide or dioxide: $C_2H_2 + CO \quad H_2O + 3C$.

Swedish lampblack costs 16*s*. to 20*s*. per quintal, that from resinous wood 40*s*. to 52*s*., and that from lamps £8 to £20. It is used for making black varnishes, printers' ink, boot polish, &c. *Boot polish* is made by mixing lampblack with wax, molasses, turpentine, and sometimes also sulphuric acid or a little chestnut tannin extract to preserve the skin or leather. Italy imported and exported the following quantities (quintals):

		1905	1907	1908	1909	1910
Lampblack	imports . . .	1070	1986	1684	1910	2440 worth £4017
	exports . . .	50	20	56	26	97 „ £186
Boot polish	imports . . .	2335	3500	4140	4240	6900 „ £10980
	exports . . .	1786	1960	1420	1540	2518 „ £4028

petroleum residues (*see* Cracking Process, &c., p. 74). By dropping the tar into very hot retorts and evacuating the latter, oils for various industrial purposes and also gas are obtained.

The distillation is carried out in large wrought-iron vessels [1] holding several hundred quintals of tar. The old type of boiler is shown in Fig. 407, but preference is now given to horizontal stills, which are sometimes multitubular, like locomotive boilers, in order to obtain more homogeneous and more rapid heating. It will be seen in the figure that direct-fire heat is used (at *b*); the mass is mixed at intervals by means of a stirrer or of a steam-jet introduced at *x* and subdivided on the arched base of the still by a number of pipes, *z*. The tar enters at *r*, and at the end of the operation the pitch is discharged through a much wider orifice than that marked *a*. A thermometer or pyrometer is inserted at *v*, while *t* serves as exit for the vapours, which are condensed in a coil surrounded by cold water in the case of the first products and by hot water in that of the last products; these are collected in order of density in a number of small receivers, from which they are passed to large store-tanks. The stills are arranged in batteries under light roofs open at the sides so that the damage in case of fire or explosion may be minimised, the further precaution being taken of placing the fire hearths outside in the open. When the products formed at 270° are distilled over, the yield is increased and the pitch rendered more liquid, and so prevented from charring, by introducing a current of superheated steam, this removing various substances (anthracene oil) which would otherwise remain in the pitch. The latter is then discharged, while hot, into old disused steam boilers so as to avoid contact with the air, which might ignite the mass; when almost cold but still fluid, it is run into shallow vessels or pits dug in the earth and allowed to solidify. With a still holding 300 to 400 quintals, each distillation (including charging and discharging) lasts about 4 days. Distillation in a vacuum saves time (less than 30 hours being required for 200 quintals) and lessens repairs.

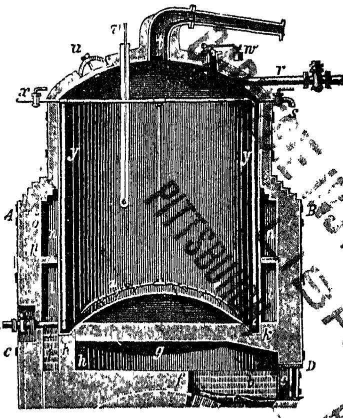


FIG. 407.

In order to avoid decomposition of the products distilling at high temperatures and to make the *distillation continuous* and thus increase the output and economise fuel, Wernecke (Ger. Pat. 201,372, 1907) has proposed the use of a conical, stepped still, *A*, fitted with a number of superposed peripheral channels, *E*, inside (Fig. 408). The cover, *B*, is fitted with a vapour outlet, *b*, and a pipe, *a*, for the continuous introduction of the tar (which first passes through a heater, where the water and light oils are distilled). The latter enters the uppermost channel, *E*, and overflows into the lower channels, gradually diminishing in volume owing to the distillation of various products; the more or less liquid pitch is discharged at *d*. The vapours of the medium oils pass through the upper orifice, *b*, to refrigerators, but those of the heavy oils from the lower channels are collected by the perforated pipe, *DF*, which is provided with a cap, *G*, and is surrounded by metal gauze, and carries them through *c* to refrigerators. The still is heated by the

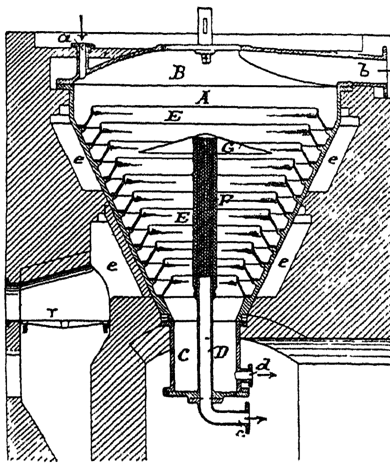


FIG. 408.

[1] The rapid wear of the iron vessels and coils is due especially to HCl, NH_3, H_2S, HCN, &c., formed by the dissociation at high temperatures of chlorides (*e.g.* ammonium chloride, dissociating at 360°), sulphides, cyanides &c., and perhaps also by certain electrolytic processes. The base of the still is often 18 to 20 mm. in thickness. Cast-iron coils last better than those of wrought-iron, and are composed of superposed straight tubes connected at alternate ends by semicircular pipes of cast-iron.

gases from the hearth, *r*, which circulate in the flues, *e*. The distillation is only interrupted once in 4 to 8 weeks to allow of the removal of the coke deposited on the inner surface of the still. Although the total capacity of the channels is only 600 kilos of tar, the daily output is equal to that of a still of the old type holding 2500 to 3000 kilos. Such a still also serves well for the distillation of *lubricating oils* from petroleum residues.

In order to prevent the tar from frothing, it is necessary first to free it from water as completely as possible. This is done by maintaining the mass in open vessels for some hours at 40° to 50° or by adding quicklime or gypsum as a dehydrating agent.[1]

The products which distil below 110° at ordinary pressure (sp. gr. 0·900 to 0·920) are somewhat similar to the ammoniacal liquor of gasworks, and consist of a more or less coloured liquid on which floats an oil containing a little benzene and toluene.

The second portion which is collected is that distilling between 110° and 210°, this forming the so-called *light tar-oils* (sp. gr. 0·935 to 0·995).

From 210° to 240° the *phenols* or *medium oils* or *creosote oils* are collected. The next fraction consists of *heavy oils* (up to 270° ; sp. gr. 1 to 1·040), and the final one, the *anthracene oil*, passes over up to 270° (sp. gr. 1·050 to 1·095) and forms a buttery mass composed of oils and crystalline substances.

According to whether the pitch (residue) is required to be more or less liquid or solid, the distillation is suspended after the third or fourth fraction has been collected ; to render the pitch shiny, it is mixed in the still with the heavy oil remaining after the crystallisation of the anthracene. This oil is also used with other lubricants for making oil-gas (*see* p. 57), lampblack, &c.

Anthracene was very dear until a few years ago and to obtain the maximum yield the heating was continued under reduced pressure after the distillation in superheated steam.

Tar from metallurgical coke manufacture gives distillation products differing in their proportions from those of coal-tar, and even with the latter the tar from the hydraulic main (p. 43) is richer in pitch and poorer in light oils than the tar from the condensers and separators. The tar from coke factories contains more light oils and less water than that from gasworks, and distils more regularly and more rapidly.[2]

STATISTICS AND PRICES. The price of tar varies considerably with the locality, quality, season, demand, &c., the limits being about 1*s*. 7*d*. and 3*s*. 2*d*. per quintal. In Germany the price reached the maximum of 4*s*. 6*d*. per quintal in 1885 and fell to 1*s*. 8*d*. in 1898 ; it now varies from 2*s*. 4*d*. to 2*s*. 5*d*. In 1900 the *world's production* of the various distillation products of tar was as follows : 50,000 tons of naphthalene, 24,000 of benzene, and 6000 of toluene. One-half of this output comes from coke factories and about one-third from Germany. In 1904 Germany produced 277,000 tons of tar in metallurgical coke factories (in 1908 about 632,400 tons) and 225,000 tons in lighting gasworks (in 1908 about

[1] The *separation of water* is necessary in order that the distillation may be regular ; if water is present, distillation is very slow and is accompanied by bumping and frothing. When a sufficient separation cannot be obtained by decantation from the tepid tar after standing, special methods are used. According to Ger. Pat. 161,528 the tar in the still is heated first at the surface and subsequently in lower and lower layers to the bottom. Oppenheimer and Kant remove the water by means of gypsum or cement (Eng. Pat. 12,696, 1903).

By centrifuging the tar in a non-perforated drum (as for starch, *see* p. 498), the proportion of water can be reduced to 1 to 2 per cent. In large distilleries the water is now eliminated by passing the tar from elevated tanks to the cooling coils in which the vapours of the tar are condensed ; the tar heated in this way to 50° to 60° enters a small rectifying column fitted to a large retort (150 to 200 hectols.) almost full of tar already heated to 200° and freed from water. An overflow pipe to the retort delivers tar almost without water, while from the top of the column issue steam and a considerable proportion of the light oils, which are condensed in cooling coils.

The estimation of water in tar is not easy, since when the tar is heated in a dish it readily froths and overflows. H. Beck and Rispler (1909 and 1904) allow 200 grms. of the tar to fall drop by drop from a separating funnel on to about 500 grms. of water-free heavy tar-oil contained in a flask of about 2 litres ; each drop of tar, as it falls, is instantly evaporated, and the water distilling over is condensed in the refrigerator connected with the flask and collected, together with a little tar-oil, in a graduated cylinder ; the temperature is finally raised to 300°. The cylinder is kept at a moderate temperature, so that the water separates from the oil ; its volume is then read. If much naphthalene also distils over, it is difficult to read the volume of the water ; in this case, the whole of the distillate is poured on to a small filter-paper steeped in benzene, so that only the tar-oil filters. The filter-paper is subsequently pierced and the water allowed to pass into a graduated cylinder. E. Ott, on the other hand, heats 400 grms. of tar in a copper retort, the heating being carried out from the top by means of an annular gas-pipe with orifices in its lower side.

[2] In a large German coke-tar distillery, where retorts holding 350 quintals were used, the mean yields of several years were as follows : Ammoniacal liquor, 4·27 per cent. ; light oils, 4·06 ; medium oils, 10·38 ; heavy oils, 6·11 ; anthracene oil, 13·71 ; pitch, 60·49 ; loss, 0·98. The tar distilled contained on an average 24 per cent. of matter (carbon) insoluble in benzene, and the mean cost of distilling 1000 kilos of tar was as follows : Labour, 7·7*d*. ; coal (at 1*s* 7*d*. per quintal), 14·4*d* ; steam, 4·8*d*. ; various materials, 1·4*d*. ; repairs, 3·8*d*. ; depreciation 11·5*d*. ; total, 43·6*d*. In a large distillery fitted with retorts holding 180 quintals and working at reduced pressure a larger annual output was attained, while the mean cost per ton distilled was 36·5*d*. ; the yields were as follow : Ammoniacal liquor, 3·86 per cent. ; light oils, 1·24 ; medium oils, 12·02 ; heavy oils, 8·50 ; anthracene oil,

300,000 tons); in 1908 40,000 tons of tar were imported from England (in 1909 only 18,000 tons were imported, while 35,000 tons were exported). In 1909 9659 tons of *lignite-tar* were also imported and 3078 tons exported, the total production (in 30 lignite distilleries) being 59,174 tons, which were worked up in 12 tar distilleries. In 1908 75 works in Germany distilled altogether about 812,000 tons of tar (three-fourths from cokeworks and the remainder from gasworks) of the value of £944,000. This gave products worth about £1,800,000, namely: 485,000 tons of pitch (£650,000); 36,000 tons of naphthalene (£131,000); 13,230 tons of crude and refined benzene (£110,000); 248,000 tons of heavy tar-oils, including phenol, creosote, and naphthalene oils (£500,000); 2600 tons of crude

18 68; pitch, 54 56, loss, 1 14 When tar free from water is distilled, the consumption of coal is diminished from 7 5 to 5 per cent.

The various fractions obtained in the first distillation of tar are treated as follow.

I. The **Light Oils** from gas-tar (*A*) are richer in benzene and toluene than those from coke tar (*B*), as is shown by the following mean yields obtained on fractional distillation of these oils:

	A		*B*
Crude benzene I (distilled up to 135°) .	36·12 %	...	12·66 %
,, ,, II (distilled at 135° to 165°) .	15 59 %	.	16 42 %
Phenol oils (165° to 195°)	18 01 %	. .	18 47 %
Residue (medium oils)	26 51 %	. .	49 36 %
Water and loss	3·67 %	...	3 09 %

The cost of distilling 100 kilos of light oils is as follows. 7 7*d.* for labour, 19*d.* for fuel, 8·15*d.* for steam, 4·8*d.* for repairs, and 1*s* for depreciation

The light oils are distilled and rectified in a column apparatus with stills holding 100 to 150 quintals and heated by direct fire or by superheated indirect steam, the first three fractions (up to 195°) are collected separately. The crude benzenes I and II can be purified from the small amount of phenols they contain by washing with caustic soda solution; the remaining benzene is then rectified again in order to remove the toluene, of which it may contain as much as 25 per cent (*see later*, Benzene) The phenol oils (distilled between 165° and 195°) contain appreciable quantities of naphthalene, and are therefore worked up with the medium oils.

II. The **Medium Oils** (or **Creosote Oils**) obtained by the direct distillation of gas-tar contain about 50 per cent. of naphthalene and as much as 25 per cent. of acid oils (phenols), which hold the other impurities in solution and allow of a more ready separation of a purer, crystalline naphthalene when the *crude creosote oil* is left to stand for some days in the cold; the oil is then drained away underneath and the residual naphthalene centrifuged. The medium tar-oils from metallurgical coke-tar contain about 43 per cent. of naphthalene and only 13 per cent. of acid oils, so that many impurities are deposited with the naphthalene; instead of allowing the naphthalene to crystallise, it is therefore preferable to subject the oil directly to fractional distillation, pure naphthalene being more readily obtainable from the products:

	Medium tar-oils	
	Gas	*Metallurgical coke*
Crude benzene II (to 165°)	4·15 %	1·78 %
Phenol oils (165° to 195°)	21·77 %	19·91 %
Naphthalene oil (195° to 220°) . . .	43 45 %	28·68 %
Residue	26 91 %	48·18 %
Water and loss	3·72 %	1 45 %

The residue is added directly to the heavy tar-oils, which are treated separately (*see below*). The naphthalene oil and the phenol oil are cooled so as to separate the naphthalene in large scales, which can be purified by hydraulic pressure. The residual oil which drains off contains the greater part of the phenols, which are extracted by means of caustic soda (to this may be added the alkaline solution of the phenols separated from the crude benzene), this being decanted off, treated with dilute sulphuric acid to liberate the *crude carbolic acid* as a dense black liquid. After repeated purification (by dissolving in soda and precipitating with acid) or distillation between 175° and 185°, purified carbolic acid is obtained This is crystallised by intense cooling, the white crystals obtained being freed from the last liquid impurities by centrifugation (for the complete purification of *phenol*, *see* p. 541)

If the phenols are not extracted from the creosote oils, the latter can be used for the impregnation and preservation of timber (*see later*).

The cost of working the medium oils is about the same as for light oils (*see above*).

From the residues from the carbolic acid, *i.e.* the portions insoluble in caustic soda, a little naphthalene can be recovered by distilling them with other medium oils, care being taken to warm the condensing coils so as to prevent them from becoming blocked. The purification of naphthalene is described later England exported 34,558,053 gallons (£464,828) of creosote oil in 1910 and 29,729,000 gallons (£397,431) in 1911, while the United States imported 42,608,000 gallons in 1910 and 49,311,000 gallons (£464,600) in 1911.

III. The **Heavy Oil** from gas-tar contains about 28 per cent of naphthalene and 16 per cent of acid (phenol) oils, while that from coke factories contains about 32 per cent. of naphthalene and 10 per cent. of acid oils.

Heavy tar-oil, when not redistilled in a vacuum to recover the anthracene, is used as an illuminant, or for the manufacture of lighting gas, or as fuel, or for impregnating wood. To obtain illuminating gas the oil is run in a thin stream into heated iron retorts (as in the cracking of petroleum, *see* p. 74), carbon and an oil still containing a considerable proportion of benzene being formed in addition to the lighting gas.

When these oils are used directly for heating purposes, they are pulverised under the furnaces by means of a steam-jet which introduces the necessary quantity of air.

At the Deutz gas-engine works (near Cologne), heavy tar-oil has been applied in Diesel engines. These heavy

and pure naphthalene oils (£38,825); 4020 tons of crude and purified anthracene (£32,000); 385 tons of pyridine bases (£12,680); 1000 tons of crystallised phenol (£68,000); 2080 tons of cresols, *i.e.* 90 to 95 per cent. carbolic acid (£19,440); 4700 tons of xylol, *i.e.* solvent naphtha and heavy benzene (£39,600). In addition, about £40,000 worth of ammoniacal compounds (1174 tons of ammonium sulphate, 1050 tons of ammonia, &c.) were extracted.

In England 175,000 tons of tar were treated in 1870, about 400,000 tons in 1880, more than 640,000 tons in 1886, and at the present time considerably over 750,000 tons per annum. The following quantities of *creosote oil*, extracted from tar, were consumed in England: 346,500 hectols. in 1903, 389,250 in 1904, 609,750 in 1905, and 2,520,000 in 1909, a large proportion of this being used as *carbolineum* or heavy tar-oil for the impregnation and preservation of timber and railway sleepers,[1] and for the disinfection of lavatories.

France produces now about 100,000 tons of tar per annum, Belgium about 80,000 tons, and Holland about 35,000 tons. The United States produced 280,000 tons in 1904.

oils cost in bulk about 4*s.* per quintal and have a calorific value of about 8800 to 8900 Cals.; in, *e g.* a 60 h.p. engine, 1 h.p hour would cost about 1·25*d.*

IV. The part of the tar distilling above 270° (Anthracene Oil) contains the greater part of the solid anthracene, which, after prolonged standing, is freed from the liquid impurities by hydraulic presses or filter-presses. To effect more complete removal of the liquid and also of the phenanthrene accompanying the anthracene crystals, the latter are *washed with benzine.* The residue represents 50 per cent. anthracene, the remainder being paraffins and small quantities of chrysene, pyrene, fluorene, retene, &c. The further purification of the anthracene is described later The anthracene oil which does not crystallise either serves for making *regenerated tar* by mixing with pitch, or is used as it is, under the name *carbolineum* (*see later*), for preserving wood.

V. As already indicated, the Pitch remaining in the retorts is removed carefully so as to avoid ignition. After cooling it becomes hard, since nowadays the anthracene is removed as completely as possible; if a softer pitch is required, it is mixed with a suitable proportion of waste heavy oils Pitches from different tars (wood, lignite, coal, &c) contain different amounts of phenols Pitch is used in place of natural asphalte and is improved by melting it with sulphur. Mixed with sand, it is used as asphalte for paving roads, for making bitumenised paper, asphalte pipes (with paper and sand), *briquettes* from coal-dust, and black varnish for sheet-iron and timber (*see also* Bitumen, &c., pp. 83 and 84).

[1] True *carbolineum Avenarius*, patented and improved (Ger Pat. 46,021 of 1888), does not appear to contain creosote oil, naphthalene, anthracene, or phenols. To render it more dense (sp. gr. 1·2), less inflammable and of a less unpleasant odour, it is gently heated and treated with a current of chlorine; it contains also a little zinc chloride According to the quality the price varies from 12*s.* to 36*s.* per quintal

Preservation of Wood. Timber, railway sleepers, telegraph poles, &c., especially when in contact with the ground, are injured and become unusable in a few years owing to the attacks of various moulds and micro-organisms (*Merulius lacrimans, Polyporus vaporarius*, &c). Even when hard wood is used it gradually becomes considerably attacked. Telegraph poles and railway sleepers have been successfully treated by smearing with pitch or bitumen the parts which come into contact with the earth, and superficial charring of the wood at the points most subject to attack has also been tried. Formerly much use was made of the method of mineralising wood. Concentrated and more or less hot solutions of various salts (ferrous or copper sulphate, zinc chloride, &c.) are forced into the pores of the wood under pressure; or the wood is heated in a large autoclave, which is then evacuated to remove all the air and water from the pores and subsequently filled with the salt solution, which thus impregnates the wood completely. But the process which gives the best results and has become widely used in recent years is that of Bethell, which consists in the complete impregnation of the timber with heavy tar-oils (crude creosote oil); these contain phenols, cresols, &c , which have a marked disinfecting action. In Italy this process has been applied for some years, and is carried out, not in autoclaves, but in open vessels, such as are used in America, the treatment being completed in zinc solutions according to the improvements of the Giussani patents. The beams are first immersed for 5 to 6 hours in a bath of fused masut (*see* p. 74) kept at 160° to 170°, by which means the wood is deprived of its air and water and sterilised; they are then passed into a cold vessel containing medium tar-oil (the portion distilling at 210° to 240° and having an acidity of 25 per cent. due to various phenols) where, after 20 to 30 minutes cooling, the oil penetrates the pores to a depth of 1 cm. or more. The wood is finally left for 3 to 4 hours in a cold, concentrated solution of zinc chloride, which forces the oil further in and forms a thin superposed layer in the pores (the wood absorbs as much as 15 per cent. of the zinc chloride solution). Thus treated, wood resists the action of weather, water, and soil for 15 to 20 years, soft wood being as resistant as hard.

The German railways require that every sleeper, 2·7 × 0·26 × 0·16 metres, shall contain 7 kilos of creosote oil. In order to economise tar-oil, Ruping's process is often used. This consists in creating an air pressure of 5 atmos. in the autoclave containing the wood and then introducing the creosote oil at 10 atmos. pressure When the pressure in the autoclave subsequently falls off, the excess of oil is forced out by the air compressed in the pores, the latter remaining coated inside with a thin layer of oil. In this way 2 kilos of creosote oil give the same sterilising effect. Seidenschnur (1909) holds that the phenolic (acid) components of the creosote oil are unnecessary, since the phenols are not antiseptic in solutions of oil; he prefers the use of aqueous emulsions containing 2 per cent. of anthracene oils (which are devoid of phenols), every sleeper containing after impregnation 0 8 kilos of anthracene oil, which preserves the wood, as well as 7 kilos of creosote oil. Good results have also been obtained with heavy petroleum oils heated to 200° with 2 per cent. of sulphur and then mixed with 40 per cent. of creosote oil.

According to Friedmann and Heidenstam, wood is preserved well by impregnating it with calcium cresolate (soluble in water) and then precipitating calcium carbonate and cresol in the pores by simple exposure of the wood to air or, better, to fumes rich in carbon dioxide (Danish Pat. 12,419 of 1909).

For the **Disinfection and Deodorisation of Urinals**, continuous rinsing with water may be replaced with advantage by brushing on a thin layer of a mixture of tar-oils of various compositions (heavy tar-oils mixed with heavy mineral oil, &c.). This mixture should answer the following requirements: sp. gr. 0·990 at most; b.pt. 165° at least; it should remain liquid at 0° and should not separate into different layers on standing; it should not contain soap, alcohols, or free mineral acids; at least 75 per cent. should distil at 350°; it should contain at least 7 per cent. of cresol.

Italy's imports and exports of tar are as follow:

		1906	1907	1908	1909	1910
Vegetable tar	Imports, quintals	9600	16,600	16,110	15,045	21,825 (£21,826)
	Exports „	367	722	1,051	1,857	1,061 (£1,061)

Perkin calculated the value of the final products of the complete and rational treatment of 9,000,000 tons of coal (costing £5,400,000) to be as follows: dyes, £3,350,000; ammonium sulphate (195,000 tons), £1,960,000; pitch (325,000 tons), £365,000; creosote oil (1,125,000 hectols.), £208,000; crude carbolic acid (45,000 hectols.), £220,000; coke, £2,400,000. Total, £8,503,000, exclusive of the 30 cu. metres of gas per ton of coal carbonised.

BENZENE (or Benzol), C_6H_6. This was discovered by Faraday in 1825 in the liquid obtained on compressing illuminating gas, but the more abundant source, tar, was found by Hofmann in 1845.

It is obtained pure by the dry distillation of benzoic acid with lime, and then forms a colourless, mobile, highly refractive liquid of sp. gr. 0·8841 at 15°, b.pt. 80·4°, and m.pt. + 5·4°; it burns with a luminous, smoky flame. The commercial product contains thiophene and traces of carbon disulphide, which can be eliminated in various ways, *e.g.* with moist ammonia (Schwalbe, Ger. Pat. 133,761) which separates insoluble oil drops, or with boiling mercuric acetate or sulphur chloride; according to Ger. Pat. 211,239, formaldehyde, acetaldehyde, or phthalic anhydride may also be used, all these substances combining with thiophene. Benzene dissolves resins, fats, sulphur, rubber, gutta-percha, camphor, &c., it mixes with alcohol, ether, acetone, &c., and is almost completely insoluble in water.

The preparation of *artificial benzene*, starting with petroleum, was described on p. 75. Benzene forms the prime material for many varied syntheses of aromatic compounds, such as nitrobenzene, aniline, &c., and of dyes (also nowadays of artificial indigo). It is used as a solvent for fats and for purifying many organic compounds; the addition of 15 per cent. of benzene to the alcohol used with an Auer mantle for lighting purposes results in a saving of 27 per cent. of the alcohol. Large quantities of 90 per cent. benzene are now used for carburetting illuminating gas to which water-gas has been added (*see* p. 52). It is also employed for dissolving rubber and lacs for making linoleum, for removing fat from bones, and for automobile engines.[1]

At one time it was obtained exclusively from gas-tar, this yielding also larger quantities of toluene, the uses of which were limited. After 1880, when the tendency was to obtain increased yields of illuminating gas by raising the temperature of carbonisation of the coal, the quantity of tar diminished, as also, in still greater proportion, did the amount of benzene. In 1882, the price of benzene, then in great demand by dye manufacturers, exceeded £12 per quintal. It was then that attention was turned to the recovery of the tar from metallurgical coke factories, but although this tar is obtainable in large amounts, it is very poor in benzene, most of which escapes with the gases and is wasted in the combustion furnaces. Darby was the first to suggest the recovery of the benzene from the gases of the coke furnaces; and nowadays these gases, before being burnt, are either strongly cooled to condense the benzene or washed with slightly volatile tar-oils, in which the benzene dissolves and from which it is recovered by subsequent heating.[2] As a result

[1] When sufficiently cheap, it may replace petroleum benzine in engines. But it requires more oxygen (air) for its combustion, and, in order to prevent it from freezing in winter, should contain a little toluene.

[2] The manufacture of crude benzene from tar was described on p. 529. The rectification of the hydrocarbons contained in the first distillate from the tar (light oils) is regulated so as to give three fractions: (1) *commercial 90 per cent. benzene I* of sp. gr 0 885 at 15° (90 per cent. of this distils at 100° and 100 per cent. at 120°; it contains about 20 per cent. of toluene; 120° is termed the *dry-point* of the benzene); (2) *50 per cent. benzene II* with sp. gr. 0·880 (50 per cent. of this distils at 100° and 90 per cent. at 120°); (3) *heavy benzene* or *solvent naphtha* with sp. gr 0·875 (20 per cent. of this distils at 130° and 90 per cent. at 160°; it serves as a good solvent for rubber.)

An apparatus suitable for the rectification of crude benzene is that of Hirzel described and illustrated on p. 76, or the similar one of Heckmann shown on p. 140, but having a still with a smaller base in the form of a short horizontal cylinder. From the 90 per cent. benzene, *pure benzene* can be obtained by further rectification

of this process, the production of benzene became more than ten times that of *toluene*, the price, which was £2 to £3 per quintal in the period 1885–1896, falling to 20*s*. to 24*s*. in 1898–1910. Pure thiophene-free benzene costs about 1*s*. 6*d*. per kilo; the puriss. product, obtained from benzoic acid, is sold at 32*s*. per kilo.

The German association for the sale of products of distillation of coal (ammonia, &c.) sold about 15,000 tons of benzene in 1903 and nearly 16,200 tons (90 per cent.) in 1904. In 1870 Germany produced 1200 tons of benzene, in 1890 4500 tons, in 1896 7000 tons, in 1901 28,000 tons, and in 1904 37,000 tons, of which 80 per cent. was used in dyeworks and about 10 per cent. in the manufacture of illuminating gas. England exported 2,672,770 gallons of benzene and toluene in 1910 and 4,068,740 gallons (£139,193) in 1911.

Italy imported the following quantities of benzene (including small amounts of toluene and xylene): 37 tons in 1906, 430 in 1907, 463 in 1908, 636 in 1909, 600 tons (£10,800) in 1910.

TOLUENE (or **Methylbenzene**), $C_6H_5 \cdot CH_3$, is formed by the dry distillation of balsam of Tolu and of various resins, and is obtained in appreciable quantities by the distillation of tar (*see above*). It boils at 110°, does not solidify even at − 28°, and has the sp. gr. 0·87 at 15°. It occurs to the extent of 10 to 15 per cent. in crude benzene I and of 25 per cent. or more in crude benzene II.

Crude toluene is purified from the hydrocarbons of the fatty series which always accompany it (and are not eliminated by rectification) by washing it with hot sulphuric acid containing a little nitric acid, the olefines being thus polymerised and the thiophene decomposed. It may also be purified by heating with sodium.

Commercial pure toluene gives 99 per cent. of distillate below 112° and 95 per cent. between 108° and 110° (two drops per second). It does not colour on protracted shaking with concentrated sulphuric acid, and if 90 c.c. of toluene and 10 c.c. of nitric acid (44° Bé.) are shaken together for some minutes in a tall glass-stoppered cylinder, the nitric acid should become only a transparent red and not a greenish black and should not thicken.

Toluene is used in the manufacture of dyes, pharmaceutical products, perfumes, &c., and, during recent years, of trinitrotoluene (*see later*), which is used in large quantities as an explosive.

The pure toluene of commerce costs in Germany about 36*s*. per quintal for large quantities.

XYLENES (**Dimethylbenzenes**), $C_6H_4(CH_3)_2$. Xylene obtained from tar contains the three isomerides, *o*-, *m*-, and *p*-, metaxylene being present to the extent of 70 to 80 per cent. They cannot be separated by fractional distillation owing to the small differences between their boiling-points (*o*- 142°; *m*- 139°; *p*- 138°).

Treatment with concentrated sulphuric acid in the cold, however, converts the *o*- and *m*-compounds into the corresponding sulphonic acids, the *p*-xylene remaining unchanged. The sodium salt of *o*-toluenesulphonic acid crystallises more readily than that of the *m*-compound, so that the three hydrocarbons can be separated. With oxidising agents, the xylenes give phthalic acids (*see later*).

It is mostly *m*-xylene which is used in the manufacture of dyes, and the commercial product costs about £7 8*s*. per quintal; chemically pure *m*-xylene is sold at 14*s*. per kilo (chemically pure *o*-xylene costs 72*s*. per kilo and the *p*-compound 40*s*.).

ETHYLBENZENE, $C_6H_5 \cdot C_2H_5$, is obtained by Fittig's synthesis (*see* p. 526) and gives benzoic acid on oxidation (difference from the xylenes).

and freezing, the mass of benzene crystals being pressed and centrifuged to remove the liquid toluene and higher homologues.

Commercial benzene obtained from coke-furnace gases contains 85 per cent. of benzene, 11·7 per cent. of toluene, 1·4 per cent. of xylene, and 1·87 per cent. of naphthalene and other products. Gas-tar gives less than 1·5 per cent of benzene and toluene together, most of these products (93 per cent. of the amount obtained on distilling coal) remaining in the gas (as much as 45 grms. per cu. metre; the gases from metallurgical coke contain only 20 grms.). Every ton of Westphalian coal converted into coke yields about 4 kilos of benzene and 0·9 kilo of toluene; other coals give only about 1·5 kilos of these two products together.

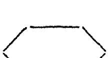
The *testing of commercial benzene* is carried out by determining its density and by fractionally distilling it; 100 c.c. are distilled in an ordinary flask with a side-tube (*see* p 3) and heated on a metal gauze with a flame so adjusted that two drops distil over per second; the flame is removed for a minute before changing the cylinders in which the separate fractions (100°, 120°, 130°, 160°) are collected. In some cases a nitration test is made, note being taken of the yield of nitrobenzene, purified by steam, and then rectified (*see later*, Nitrobenzene). The addition of petroleum spirit to benzene is detected by the lowering of the density; also petroleum spirit does not dissolve tar-pitch or picric acid, which are readily soluble in benzene. Further, the latter reacts vigorously with concentrated nitric acid, which does not attack petroleum spirit.

TRIMETHYLBENZENES, $C_6H_3(CH_3)_3$ (*see* Table, p. 527). The following isomerides are known:

(*a*) **Mesitylene** (symm. 1 : 3 : 5-) is a liquid of pleasant odour boiling at 165°. Its constitution is proved by its synthesis from acetone or allylene, by the fact that it does not form isomeric compounds by further substitution in the nucleus, and by its oxidation products: nitric acid oxidises the three side-chains successively and chromic acid simultaneously.

(*b*) **Pseudocumene** (asymm. 1 : 2 : 4-) is prepared from bromo-p-xylene (1 : 4 : 2) or bromo-m-xylene (1 : 3 : 4) by Fittig's synthesis, which indicates its constitution. It is obtained in small proportion from the distillation products of tar, and is separated from mesitylene by conversion into the slightly soluble sulphonic acid (*see* Xylenes).

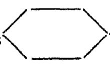
(*c*) **n-Propylbenzene**, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH_3$. The constitution of this compound is shown by the facts that it yields benzoic acid when oxidised and that it is obtained synthetically (Fittig) from propyl iodide and bromobenzene or from benzyl chloride, $C_6H_5 \cdot CH_2Cl$, and zinc ethyl.

(*d*) **Isopropylbenzene** (or *cumene*), —$CH(CH_3)_2$, also gives benzoic acid on oxidation, and is formed from benzene with either isopropyl iodide or normal propyl iodide (in the latter case aluminium chloride is necessary to cause molecular rearrangement); it is obtained also on distilling cuminic acid, $C_6H_4(C_3H_7) \cdot CO_2H$, or by the interaction of benzal chloride, $C_6H_5 \cdot CHCl_2$, and zinc methyl.

TETRAMETHYLBENZENES, $C_6H_2(CH_3)_4$. The best known of these are the following:

(*a*) **Durene** (1 : 2 : 4 : 5) or s-tetramethylbenzene, which is found, together with isodurene, in tar; it is a solid, has a smell resembling that of camphor, and is prepared synthetically from toluene and methyl chloride.

(*b*) and (*c*) **Isodurenes**, two isomerides being known (1 : 2 : 3 : 4 and 1 : 2 : 3 : 5) (*see* Table, p. 527).

(*d*) **p-Methylisopropylbenzene** or *cymene*, CH_3—$CH(CH_3)_2$, is a liquid of pleasant odour, b.pt. 185°. It occurs naturally in cumin oil (from *Cuminum cyminum*) and in various essential esters, and it can be prepared by heating camphor with phosphoric anhydride or by the interaction of oil of turpentine and iodine. On oxidation it yields various acids.

(*e*) **m-Isocymene** is found in resin oil.

Hexamethylbenzene (*mellithene*), $C_6(CH_3)_6$, m.pt. 164°, is a stable compound and can be neither nitrated nor sulphonated, owing to the absence of hydrogen atoms from the nucleus. When oxidised with potassium permanganate, it gives **Mellitic Acid**, $C_6(CO_2H)_6$.

HYDROCARBONS WITH UNSATURATED SIDE-CHAINS

As far as the nucleus is concerned, these compounds behave like true benzene derivatives, whilst by means of the unsaturated side-chain they give all the reactions of unsaturated methane derivatives.

STYRENE, $C_6H_5 \cdot CH : CH_2$, occurs in storax and is formed on heating cinnamic acid, which loses CO_2:—$C_6H_5 \cdot CH : CH \cdot CO_2H = CO_2 + C_6H_5 \cdot CH : CH_2$. It is a liquid of pleasant odour boiling at 146°, and tends to polymerise to **Metastyrene**. Styrene combines with bromine, iodine, hydrogen, &c., in the same way as olefines do. When it is treated with nitric acid, a nitro-group is introduced into the side-chain, giving **Nitrostyrene**, $C_6H_5 \cdot CH : CH \cdot NO_2$, the constitution of this being shown by its formation from benzaldehyde and nitromethane: $C_6H_5 \cdot CHO + CH_3 \cdot NO_2 = C_6H_5 \cdot CH : CH \cdot NO_2 + H_2O$.

Styrene serves for the synthesis of anthracene (*q.v.*).

PHENYLACETYLENE, $C_6H_5 \cdot C \vdots CH$, is a liquid of pleasant odour boiling at 142°, and is prepared by converting acetophenone, $C_6H_5 \cdot CO \cdot CH_3$, by means of PCl_5, into the dichloro-derivative, $C_6H_5 \cdot CCl_2 \cdot CH_3$, and eliminating 2HCl from the latter by the action of potassium hydroxide.

It is also obtained by the cautious distillation of **Phenylpropiolic Acid**, $C_6H_5 \cdot C \vdots C \cdot CO_2H$. Like acetylene, it forms metallic compounds; treatment with concentrated sulphuric acid results in the addition of H_2O, subsequent dilution with water giving acetophenone.

B. HALOGEN SUBSTITUTION PRODUCTS OF BENZENE

Halogens act on benzene and its homologues, replacing one or more atoms of hydrogen and forming colourless liquids (sometimes crystalline substances) which are heavier than water, distil unchanged, and dissolve in alcohol and in ether.

In aromatic hydrocarbons, a halogen in the benzene nucleus is held much more firmly than one in a side-chain and cannot be replaced by hydroxyl by the action of silver hydroxide or by the amino-group by treatment with ammonia; only by sodium or sodium alkoxide at about 200° can the halogen be eliminated.

The chlorine in the nucleus of chlorotoluene is united as firmly as in chlorobenzene, whilst the chlorine in benzyl chloride is readily replaceable, just as is the case with that in methane derivatives. To ascertain whether the halogen is present in the nucleus or in the side-chain, the oxidation products are studied; thus, chlorotoluene gives chlorobenzoic acid, $C_6H_4Cl \cdot CO_2H$, whilst benzyl chloride yields benzoic acid.

For distinguishing isomeric halogen derivatives, the same methods are used as for the xylenes, &c.

In order to be able to name aromatic derivatives the more readily, the following names are given to the more common of the different groups or *aromatic residues* (known as aryl radicals and denoted generally by Ar): $-OH$, phenolic; $-CO_2H$, carboxyl; $-O \cdot CH_3$, methoxy; $-C_6H_5$, phenyl; $-CH_2 \cdot C_6H_5$, benzyl; $-CO \cdot C_6H_5$, benzoyl; $-CN$, nitrile; $-SO_3H$, sulpho or sulphonic; $-C \cdot C_6H_5$, benzenyl; $C_6H_4<^{C=}_{CO}>O$, phthalyl; $-CH \cdot C_6H_5$, benzylidene or benzal; $-C_6H_4 \cdot C_6H_4-$, diphenylene.

General Methods of Formation. (1) In direct sunlight, chlorine and bromine act on benzene, giving additive products, *e.g.* $C_6H_6Cl_6$ and $C_6H_6Br_6$, but in diffused light (best in presence of traces of iodine, aluminium chloride, antimony trichloride, &c.), substitution products are formed. With homologues of benzene, if the reaction is carried out in the cold and in the dark (or in diffused light) or in presence of iodine (which acts catalytically), the halogen only enters the benzene ring (even in the hot, if iodine is present), whilst in the hot or in direct sunlight, the substitution takes place principally in the side-chain.

(2) By heating halogenated acids with lime:

$$C_6H_4Cl \cdot CO_2H = C_6H_5Cl + CO_2.$$

(3) By withdrawing oxygen from oxygenated compounds (phenols, aromatic alcohols, ketones, acids, aldehydes) by means of PCl_5; *e.g.* $C_6H_5 \cdot OH + PCl_5 = POCl_3 + HCl + C_6H_5Cl$.

(4) By boiling with cuprous chloride or potassium iodide the diazo-compounds obtained from the corresponding nitro- or amino-compounds: $C_6H_5N:NCl = C_6H_5Cl + N_2$; $C_6H_5N:NCl + KI = KCl + N_2 + C_6H_5I$.

(5) Iodo-derivatives may be obtained by the action of iodine, iodic acid being added to oxidise the hydriodic acid which is formed. They are, however, usually obtained by process (4).

(6) *Iodobenzene*, C_6H_5I, unites with two atoms of chlorine, forming *iodosobenzene chloride*, $C_6H_5ICl_2$, digestion of which with alkali yields *iodosobenzene*, $C_6H_5I:O$, the latter, when heated or oxidised (with chloride of lime) giving *iodylbenzene*, $2C_6H_5IO = C_6H_5I + C_6H_5IO_2$ or $C_6H_5IO + O = C_6H_5IO_2$ (an explosive, crystalline compound).

Chlorination or bromination of *toluene* yields the para- and ortho-derivatives in equal quantities; the meta-derivative is obtained indirectly (from diazo-compounds).

PRINCIPAL HALOGEN DERIVATIVES OF BENZENE

Empirical formula	Name	Melting-point	Boiling-point	Specific gravity
	Chloro-derivatives			
C_6H_5Cl .	Monochlorobenzene . . .	− 42°	+ 132°	1·128 at 0°
$C_6H_4Cl_2$.	o-Dichlorobenzene (1 : 2) . .	—	179°	
	m- ,, (1 : 3) . .	—	172°	
	p- ,, (1 : 4) . .	+ 53°	172°	
$C_6H_3Cl_3$.	*v*-Trichlorobenzene (1 : 2 : 3) .	16°	218°	
	as- ,, (1 : 2 : 4) .	63°	213°	
	s- ,, (1 : 3 : 5) .	54°	208°	
$C_6H_2Cl_4$.	*v*-Tetrachlorobenzene (1 : 2 : 3 : 4)	46°	254°	
	as- ,, (1 : 2 : 3 : 5)	50°	246°	
	s- ,, (1 : 2 : 4 : 5)	137°	244°	
C_6HCl_5 .	Pentachlorobenzene . . .	86°	276°	
C_6Cl_6 . .	Hexachlorobenzene . . .	226°	326°	
	Bromo-derivatives			
C_6H_5Br .	Monobromobenzene . . .	− 31°	+ 155°	1·517 at 0°
$C_6H_4Br_2$.	o-Dibromobenzene (1 : 2) . .	− 1°	224°	2·003 at 0°
	m- ,, (1 : 3) . .	+ 1°	220°	1·955 at 20°
	p- ,, (1 : 4) . .	87°	219°	1·841 at 89°
$C_6H_3Br_3$.	*v*-Tribromobenzene (1 : 2 : 3) .	87°	—	
	as- ,, (1 : 2 : 4) .	44°	275°	
	s- ,, (1 : 3 : 5) .	120°	278°	
$C_6H_2Br_4$.	*v*-Tetrabromobenzene (1 : 2 : 3 : 4)	—	—	
	as- ,, (1 : 2 : 3 : 5)	98°	329°	
	s- ,, (1 : 2 : 4 : 5)	175°	—	
C_6Br_6 . .	Hexabromobenzene . . .	above 315°	—	
$C_6H_4Br\cdot CH_3$	o-Bromotoluene (1 : 2) . .	− 26°	181°	1·422 at 20°
	m- ,, (1 : 3) . .	− 39·8°	184°	1·410 at 20°
	p- ,, (1 : 4) . .	+ 28°	185°	1·392 at 20°
$C_6H_5\cdot CH_2Br$	Benzyl bromide . . .	liquid	198°	1·438 at 22°
	Iodo-derivatives			
C_6H_5I .	Iodobenzene	− 30°	188°	
$C_6H_4I_2$.	o-Di-iodobenzene (1 : 2) . .	+ 27°	286°	
	m- ,, (1 : 3) . .	40°	285°	
	p- ,, (1 : 4) . .	129°	285°	

BENZYL CHLORIDE, $C_6H_5\cdot CH_2Cl$, is a colourless liquid with a pungent odour, melting at − 49° and boiling at 178° ; its specific gravity at 15° is 1·113. It was first prepared by Cannizzaro in 1853, and is obtained by chlorinating boiling toluene. With potassium acetate this chloride gives the acetyl-derivative, with potassium hydrosulphide a mercaptan, and with ammonia amino-bases. On protracted boiling with water it is transformed into benzyl alcohol, while boiling with lead nitrate converts it into benzaldehyde ; when heated with finely divided copper, it loses chlorine and condenses to dibenzyl, $C_6H_5\cdot CH_2\cdot CH_2\cdot C_6H_5$.

It is used for the preparation of oil of bitter almonds and for numerous aromatic syntheses, its chlorine atom being readily replaceable.

The commercial product costs 3*s*. 5*d*. per kilo and the chemically pure 5*s*. 7*d*.

Benzyl Bromide, when treated with potassium iodide, gives **Benzyl Iodide**. These products are also formed from benzyl alcohol, $C_6H_5\cdot CH_2\cdot OH$, and halogen hydracids ; they may be converted back into the alcohol by boiling with water or potassium carbonate solution.

BENZAL CHLORIDE, $C_6H_5 \cdot CHCl_2$, and **Benzotrichloride**, $C_6H_5 \cdot CCl_3$, are obtained either by protracted chlorination of boiling toluene or by the action of PCl_5 or benzaldehyde or benzoic acid.

Benzal chloride boils at 204° and has the sp. gr. 1·295 at 16°, while the trichloride melts at − 22°, boils at 213°, and has the sp. gr. 1·380 at 14°.

Mixed halogen derivatives are known, as also is **Hexachlorohexahydrobenzene**, $C_6H_6Cl_6$. Numerous halogenated derivatives of unsaturated aromatic hydrocarbons have likewise been prepared, *e.g.* **α-Bromostyrene**, $C_6H_5 \cdot CBr : CH_2$, and **β-Bromostyrene**, $C_6H_5 \cdot CH : CHBr$.

C. SULPHONIC ACIDS

These are formed directly from the aromatic hydrocarbons by the action of concentrated or fuming sulphuric acid or of chlorosulphonic acid, $Cl \cdot SO_3H$. Improved yields are obtained in presence of mercury or ferrous sulphate, which exerts a catalytic action.

They are crystalline substances, readily soluble in water and even hygroscopic, and are separated from the excess of sulphuric acid either by means of their calcium or barium salts, which are soluble, or by saturation of the aqueous solution with sodium chloride and subsequent cooling ; in the latter case, the sodium sulphonate separates, this being decomposed with the calculated quantity of a mineral acid and the free sulphonic acid extracted with ether.

When treated with superheated steam or with hydrochloric acid, they lose the sulphonic group, the aromatic hydrocarbon being thus regenerated. With PCl_5 they form the acid chlorides, *e.g.* $C_6H_5 \cdot SO_2Cl$, which, with ammonium carbonate, yield the *sulphamides*, $C_6H_5 \cdot SO_2 \cdot NH_2$ (*see later*). On energetic reduction, *thiophenol* (phenyl hydrosulphide), $C_6H_5 \cdot SH$, is formed.

BENZENESULPHONIC ACID, $C_6H_5 \cdot SO_3H$, is obtained by the direct action of concentrated sulphuric acid on benzene: $C_6H_6 + H_2SO_4 = H_2O + C_6H_5 \cdot SO_3H$. Its barium and lead salts being soluble, it can be readily separated from the excess of sulphuric acid.

It is very stable and is not decomposed on boiling with alkali or acid (as is ethylsulphonic acid), but if heated with hydrochloric acid at 150° or with superheated steam in presence of concentrated phosphoric acid, it takes up water, giving benzene: $C_6H_5 \cdot SO_3H + H_2O = C_6H_6 + H_2SO_4$. When distilled with potassium cyanide, it forms benzonitrile, $C_6H_5 \cdot SO_3K + KCN = K_2SO_3 + C_6H_5 \cdot CN$.

When fused with alkali it forms phenol, $C_6H_5 \cdot SO_3K + KOH = K_2SO_3 + C_6H_5 \cdot OH$, while with PCl_5 it yields **Benzene Sulphochloride**, $C_6H_5 \cdot SO_3H + PCl_5 = POCl_3 + HCl + C_6H_5 \cdot SO_2Cl$ (decomposable by water).

With ammonia, ammonium carbonate, or primary or secondary amines, benzene sulphochloride gives more or less substituted **Benzenesulphonamides**, *e.g.* $C_6H_5 \cdot SO_2 \cdot NH_2$, $C_6H_5 \cdot SO_2 \cdot NHR$, $C_6H_5 \cdot SO_2 \cdot NR_2$, which crystallise well. As the tertiary amines do not give this reaction, they can be separated from other amines.

Owing to the highly acid character of the SO_2 group, the amino-group does not form salts, but its hydrogen can be replaced by metals, *e.g.* by dissolving in sodium hydroxide solution. Sulphur trioxide converts benzene into **Sulphobenzide** (*sulphone*), $(C_6H_5)_2SO_2$.

Nitration of benzenesulphonic acid yields mainly m-nitrobenzenesulphonic acid, but small quantities of the ortho- and para-derivatives are also formed.

Reduction of p-nitrobenzenesulphonic acid yields **Sulphanilic Acid** (*p-aminobenzenesulphonic acid*), $NH_2 \cdot C_6H_4 \cdot SO_3H$ (discovered by Gerhardt in 1845), which is also obtained on heating aniline with fuming sulphuric acid or on heating aniline sulphate at 200°. This acid and also the corresponding meta-acid are used in the manufacture of artificial dyestuffs, and both of them can be diazotised (*see later*).

Sulphonic compounds and their salts are of importance in the dye industry as they give dyes soluble in water and readily applied to the dyeing of textile fabrics.

Polysulphonic acids of benzene and its homologues are also known, some

of them serving for the separation of isomeric aromatic hydrocarbons (*see* Toluene).

D. PHENOLS

Phenols contain hydroxyl groups in place of one or more hydrogen atoms of the benzene nucleus. They have a characteristic odour (phenol, thymol), and certain of them are partially soluble in water, while all of them are soluble in alcohol and in ether; they distil unchanged and have a more or less marked antiseptic action.

Their properties resemble, to some extent, those of tertiary alcohols and those of weak acids. Thus, ethers are formed by the action of alkyl halogen compounds on the sodium derivatives of the phenols, anisole, $C_6H_5 \cdot OCH_3$, and phenyl sulphate, $C_6H_5 \cdot O \cdot SO_3H$, being obtained in this way; the latter compound is readily hydrolysed. They are, however, stable towards oxidising agents, nitric acid forming substitution products. The hydroxyl group is with some difficulty replaced by chlorine by the action of PCl_5. They act as weak acids, but with alkalis form stable salts, which are soluble in water, are decomposed even by carbonic acid, and show only slight electrical conductivity.

Halogens and nitric acid replace the benzene hydrogen of phenols more *easily* than that of benzene itself or its homologues, so that even in dilute solution phenol can be precipitated quantitatively as tribromophenol by the action of bromine water.

If the hydroxyl group is joined to a side-chain and not to the benzene nucleus directly, the compound is an aromatic alcohol and not a phenol.

Oxidation of homologues of phenol yields hydroxy-acids, the side-chain being oxidised while the phenolic groups remain intact.

When distilled with zinc dust, phenols give the corresponding aromatic hydrocarbons.

In aqueous neutral solution, phenols give a violet, green, or other coloration with ferric chloride, calcium hypochlorite, or, in some cases, iodine. In general, they exert a reducing action.

With nitrous acid, phenols form isonitroso-derivatives (oximes), and, in presence of concentrated sulphuric acid, intensely coloured solutions are formed which are turned blue by potash (*Liebermann's reaction*). The sodium or potassium derivatives of the phenols (*phenoxides*), with carbonic acid (or $(CCl_4 + KOH)$ give aromatic hydroxy-acids:

$$C_6H_5 \cdot OH + CO_2 = OH \cdot C_6H_4 \cdot CO_2H.$$

With chloroform and sodium hydroxide, they yield the corresponding aldehydes.

They react with diazo-compounds and various other compounds forming colouring-matters (*see later*). The action of zinc chloride (or calcium chloride) and ammonia on phenols results in replacement of the OH by NH_2.

(*a*) MONOHYDRIC PHENOLS

These are found alone or together with polyhydric phenols, and partly in the form of ethers (*e g.* guaiacol, $OH \cdot C_6H_4 \cdot OCH_3$, cresol, &c.) in the tar obtained by the dry distillation of wood or coal. They are separated from the tar-oils by means of caustic soda, which renders them soluble, and, after separation, are set free by mineral acid and subjected to fractional distillation.

They are also obtained industrially by fusing salts of sulphonic acids with alkali (in iron vessels; in the laboratory silver vessels are used):

$$C_6H_5 \cdot SO_3K + 2KOH = C_6H_5 \cdot OK + K_2SO_4 + H_2O.$$

If the nucleus contains chlorine atoms, these are also substituted by hydroxyl groups by this reaction.

THE MOST IMPORTANT PHENOLS

Formula	Name	Melting-point	Boiling-point	Specific gravity
$C_6H_5 \cdot OH$	Phenol (hydroxybenzene)	+ 42·5°	183°	1·039 at 58·5°
$CH_3 \cdot C_6H_4 \cdot OH$	o-cresol or o-hydroxytoluene (1-methyl-2-hydroxybenzene)	30	191	1·043 at 23°
"	m- " " (1- " 3- ")	4	203	1·035 at 13·6°
"	p- " " (1- " 4- ")	36	202	1·034 at 18°
$(CH_3)_2C_6H_3 \cdot OH$	o-Xylenol (*v*) (1 : 2-dimethyl-3-hydroxybenzene)	73	213	—
"	o- " (*as*) (1 : 2- " 4- ")	65	222	—
"	m- " (*v*) (1 : 3- " 2- ")	49	—	—
"	m- " (*as*) (1 : 3- " 4- ")	25	209	1·036 at 0°
"	m- " (*s*) (1 : 3- " 5- ")	63	218	—
"	p- " (1 : 4- " 2- ")	75	209	0·971 at 81°
$C_2H_5 \cdot C_6H_4 \cdot OH$	o-Ethylphenol (1-ethyl-2-hydroxybenzene)	liq.	203	1·037 at 0°
"	m- " (1- " 3- ")	− 4	214	1·040 at 0°
"	p- " (1- " 4- ")	+ 45	219	—
$(CH_3)_3C_6H_2 \cdot OH$	Mesitol (1 : 3 : 5-trimethyl-2-hydroxybenzene)	71	219·5	—
"	Pseudocuminol (1 : 2 : 4-trimethyl-5-hydroxybenzene)	73	235	—
"	Hemimellithenol (1 : 2 : 3- " 5- ")	81	—	—
$C_3H_7 \cdot C_6H_4 \cdot OH$	p-Propylphenol (1-propyl-4-hydroxybenzene)	liq.	232	1·009 at 0°
$(CH_3)_2CH \cdot C_6H_4 \cdot OH$	p-Isopropylphenol (1-isopropyl-4-hydroxybenzene)	61	229	—
$(CH_3)_4C_6H \cdot OH$	Prehnitenol (1 : 2 : 3 : 4-tetramethyl-4-hydroxybenzene)	87	266	—
"	Durenol (1 : 2 : 4 : 5-tetramethyl-3-hydroxybenzene)	117	250	—
$(CH_3)_2{:}CH \cdot C_6H_3(CH_3) \cdot OH$	Carvacrol (1-methyl-4-isopropyl-2-hydroxybenzene)	0·5	237	0·979 at 20°
"	Thymol (1- " 4- " 3- ")	50	232	0·982 at 9·6°
$(CH_3)_3C \cdot C_6H_4 \cdot OH$	p-tert. Butylphenol (1-tert. butyl-4-hydroxybenzene)	99	238	0·908 at 114°
$(CH_3)_5C_6 \cdot OH$	Pentamethylphenol (1 : 2 : 3 : 4 : 5-pentamethyl-6-hydroxybenzene	125	267	—
$(C_2H_5)(CH_3)_2C \cdot C_6H_4 \cdot OH$	tert. Amylphenol (1′ : 1′-dimetho-1-propyl-2-hydroxybenzene)	94	266	—
$(C_2H_5 \cdot CH_2)_2CH \cdot C_6H_4 \cdot OH$	Heptylphenol (1′-propo-1-butyl-4-hydroxybenzene)	71	281	—
$(C_6H_{13})(CH_3)CH \cdot C_6H_4 \cdot OH$	Octylphenol (1′-metho-1-heptyl-4-hydroxybenzene)	liq.	—	—
$C_{16}H_{33} \cdot C_6H_4 \cdot OH$	Hexadecylphenol	77·5	260 (16 mm.)	—
$C_{18}H_{37} \cdot C_6H_4 \cdot OH$	Octadecylphenol	84	277 (15 mm.)	—

Phenols are formed by boiling diazo-compounds (*see later*) with water in dilute sulphuric acid solution :

$$C_6H_5 \cdot N_2Cl + H_2O = N_2 + HCl + C_6H_5 \cdot OH.$$

Also, when benzene is oxidised with H_2O_2 or with oxygen in presence of aluminium chloride, phenols are obtained.

Chlorine atoms or amino-groups joined directly to the nucleus can be replaced by hydroxyl-groups by the action of sodium hydroxide, but only when the nucleus contains also strongly negative groups, *e.g.* NO_2.

PHENOL (Carbolic Acid), $C_6H_5 \cdot OH$, was first discovered by Runge in tar and occurs, to a small extent, in combination in urine.

It is separated from tar-oils (*see* p. 530) by treatment with caustic soda solution (sp. gr. 1·09) and agitation by a current of air ; steam is passed through the decanted alkaline solution of phenol, this removing the naphthalene, &c. The phenol is then liberated by H_2SO_4 or CO_2 (*e.g.* flue gases) and washed several times with water, *crude carbolic acid* (containing 40 per cent. of phenol, the rest creosote, &c.) of sp. gr. 1·05 to 1·06 being thus obtained.[1]

This is purified by repeated distillation between 175° and 185° or, better, rectification until it crystallises at the ordinary temperature and no longer turns red in the air. To free it from final traces of cresol, it is diluted with 12 to 15 per cent. of water and the hydrate crystallised at −8° to − 10° (cresol hydrate crystallises at 20°), centrifuged and distilled until a strength of 99 per cent. is attained ; repetition of the operation and of the distillation (in earthenware vessels) gives chemically pure phenol. Minimal quantities of water prevent crystallisation at the ordinary temperature.

The low price of benzene renders practicable the industrial synthesis of phenol ; by means of fuming sulphuric acid the sulphonic acid is formed, this being then fused with one-half of its weight of caustic soda: $C_6H_5 \cdot SO_3Na + 2NaOH = H_2O + Na_2SO_3 + C_6H_5 \cdot ONa$. The addition of acid then liberates *pure synthetic phenol*, which has very little smell and is suitable for the manufacture of picric and salicylic acids, &c.

Pure phenol crystallises in long, colourless needles melting at 42·5° and boiling unchanged at 183° ; it has a specific gravity of 1·084, dissolves in 15 parts of water at 16°, and is readily soluble in alcohol or ether. It has a characteristic odour, is poisonous, and on account of its great antiseptic power is largely used as a disinfectant in medicine and surgery [2] ; in many cases it is, however, replaced by other antiseptics (corrosive sublimate, cresols, &c.) which have not the unpleasant odour of phenol. The maximum antiseptic action of phenol is exerted in aqueous solution and in presence of acid, owing to its partial dissociation into the ions $C_6H_5O^1$ and $H^{\cdot}$; according to Pflügge, when dissolved in pure alcohol or in oil, it has no antiseptic action, since it is then not dissociated.

It dissolves in caustic alkali solutions (forming *phenoxides, e.g.* $C_6H_5 \cdot ONa$), but not in those of alkali carbonates. With formaldehyde it forms resinous condensation products (*artificial sealing-wax :* Resit, 1909).

A pine splinter, moistened with hydrochloric acid, is coloured bluish green by phenol.

[1] **Testing of Carbolic Acid** Commercial pure phenol melts at 39°, other pure forms melting at 30° to 35° and boiling at 183° to 186°. When pure, phenol should dissolve completely to a clear solution in 15 parts of water and should leave no residue on evaporation. Phenol which does not crystallise at the ordinary temperature contains at least 10 per cent. of higher phenol liquors. The exact quantitative estimation of pure phenol (not containing cresols, which behave like phenol) is effected by transforming it into tribromobenzene by Koppeschaar's method. There is no characteristic reaction for distinguishing the phenols from cresols, but the latter are the less soluble in water. An approximate method, which is used in practice, and is suggested also in the German Pharmacopœia, for determining the phenol-content of crude carbolic acid is as follows : 10 vols. of the product are shaken for a long time with 90 vols. of sodium hydroxide solution (sp. gr. 1·079) in a graduated cylinder and then left to stand until two layers separate ; the volume of the undissolved non-phenol is then read off and, after this has been removed, the residue is acidified with HCl and NaCl added to separate the whole of the phenol, the volume of which is subsequently measured.

[2] The action of **Antiseptics** or **Disinfectants** (*see also* p. 127) depends on the chemical character of the antiseptic substance and partly on the quantity and nature of the substance to be disinfected. The poisonous action of disinfectants is the result of a chemical action between the proteins of the plasma of the living cells, this having varying affinities towards different antiseptics ; the concentration of the latter, the duration of the action, &c., also influence the action. With some poisonous and very dilute solutions (the limit of dilution for combination to occur between the proteins and the antiseptic varies with the nature of the latter), certain micro-organisms fix the whole of the metal of the antiseptic (*e g.* copper or mercury from their salts) ; the solution does not then react with hydrogen sulphide, while the cells of the micro-organism do so. The following Table shows the approximate doses of different antiseptics necessary to kill 10 grms. of beer-yeast (containing 30 per

The imports of carbolic acid into Italy were 888 quintals in 1903, 1574 in 1904, 1882 in 1907, and 4000 (worth £9100) in 1910. In 1905 Germany imported 55,375 quintals of crude carbolic acid at 28s. per quintal and exported 53,000 quintals of the refined product at 58s. per quintal (total, £155,200); in 1908 39,825 quintals (36,242 from England) were imported and 44,476 quintals (13,000 to Russia and 8000 to the United States) exported. In 1911 England exported 8000 tons (£162,500) of carbolic acid, while the United States imported 1150 tons (£38,000).

The *price* of commercial dark carbolic acid is about 13s. to 16s. per quintal for the 25 to 30 per cent. product; 20s. to 24s. for 50 to 60 per cent., and 30s. to 40s. for 100 per cent.; the pale acid costs 34s. to 56s.; pure redistilled crystals, m.pt. 35°, 110s.; chemically pure, 136s., and synthetic phenol, 148s. *Calcium phenoxide* costs 16s. for the 20 per cent. and 29s. for the 50 per cent. product.

Phenol forms *phenoxides* with many metals (Na, K, Hg, Cu, &c.). The alkali phenoxides, when heated with alkyl iodides, give *ethers, e.g.* **ANISOLE**, $C_6H_5 \cdot O \cdot CH_3$; **PHENETOLE**, $C_6H_5 \cdot O \cdot C_2H_5$, &c.

These ethers are neutral, very stable liquids, and, as is the case with the corresponding aliphatic compounds, boil at lower temperatures than the phenols.

They are decomposed only in energetic reactions. For instance, hydriodic acid at 140° acts on them with formation of methyl iodide, this reaction serving for the estimation of methoxy-groups in phenolic ethers (Zeisel): $C_6H_5 \cdot OCH_3 + HI = CH_3I + C_6H_5 \cdot OH$.[1]

Phenol also forms **Acid Derivatives**, *e.g.* phenylsulphuric acid, $C_6H_5 \cdot O \cdot SO_3H$, which is stable only as salts, these being obtainable, for instance, by the action of aqueous potassium pyrosulphate on potassium phenoxide. They are formed in the urine by the putrefaction of proteins, and are estimated by determining the amount of sulphuric acid liberated in

cent, *i.e.* 3 grms, of dry matter), but these numbers would doubtless require considerable modification in the disinfection of other materials:

0·05	to 0·1	grm.	carbolic acid	0·01	to 0·02	grm	silver nitrate
0·02	„ 0·04	„	formaldehyde	0·05	„ 0·1	„	zinc sulphate
1·00	„ 2·00	„	acetaldehyde	0·05	„ 0·1	„	lead acetate
0·5	„ 0·7	„	o-hydroxybenzaldehyde	0·05	„ 0·1	„	hydrochloric acid
0·2	„ 0·5	„	acetic acid	0·05	„ 0·1	„	caustic soda
0·001	„ 0·002	„	copper sulphate	0·02	„ 0·05	„	potassium permanganate
0·005	„ 0·01	„	corrosive sublimate	0·015	„ 0·03	„	chlorine
0·05	„ 0·1	„	sodium fluoride	0·5	„ 1·0	„	tannin
0·01	„ 0·025	„	hydrofluoric acid				

[1] *Estimation of Alkoxy-groups by Zeisel's Method.* When the apparatus (Fig. 409) has been found to be air-tight, 0·2 to 0·3 grm. of the substance is introduced into the flask, *A* (30 to 35 c.c.), 50 c.c. of alcoholic silver nitrate (2 grms. fused nitrate + 5 c.c. water + 45 c.c. absolute alcohol) into the two flasks, *C*, and then 10 c.c.

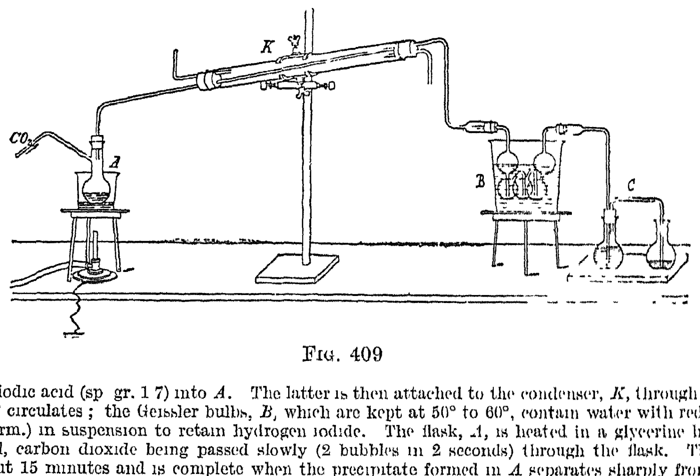


FIG. 409

of pure hydriodic acid (sp. gr. 1·7) into *A*. The latter is then attached to the condenser, *K*, through which water at 40° to 50° circulates; the Geissler bulbs, *B*, which are kept at 50° to 60°, contain water with red phosphorus (0·3 to 0·4 grm.) in suspension to retain hydrogen iodide. The flask, *A*, is heated in a glycerine bath until its contents boil, carbon dioxide being passed slowly (2 bubbles in 2 seconds) through the flask. The operation requires about 15 minutes and is complete when the precipitate formed in *A* separates sharply from the supernatant clear liquid. The total contents of the two flasks, *C*, are diluted in a beaker with 500 c.c. of water and concentrated to about one-half the volume on a water-bath. A little water and a few drops of nitric acid are then added and the liquid heated until the silver iodide separates, this being then filtered, dried, and weighed in the usual manner. Various modifications of this method have been suggested for volatile substances and especially for those containing sulphur (the substance is hydrolysed with concentrated NaOH and the products absorbed after first passing through a U-tube containing pumice moistened with $CuSO_4$; a current of air and not of CO_2 is used in this case).

the hot by dilute hydrochloric acid. Even carbonic and acetic acids form analogous compounds.

HALOGEN DERIVATIVES OF PHENOLS. The hydroxyl group of phenol facilitates the replacement of the hydrogen atoms of the benzene nucleus by halogens ; even in the cold, bromine water forms **Tribromophenol.** Chlorination can be effected by the direct action of chlorine or by sulphuryl chloride, while replacement by iodine is facilitated in alcoholic solution, or in presence of mercuric oxide (which oxidises the hydriodic acid as it is formed), or in an aqueous alkaline solution. The halogen usually assumes the ortho- or para-position with respect to the hydroxyl.

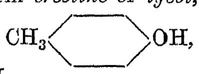
While o- or p-cresol combines with only two atoms of bromine, the action of chlorine on anisole, $C_6H_5 \cdot O \cdot CH_3$, at 60° in presence of a little iodine, yields *tetra-* or even *penta-chloroanisole*, $C_6Cl_5 \cdot OCH_3$. Halogen derivatives of phenols may also be obtained by diazotising halogenated aminophenols.

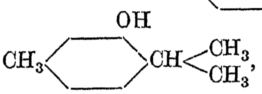
In general, they are colourless crystalline compounds of pungent odour and decidedly acid character (*trichlorophenol* decomposes carbonates) ; when they are fused with potash, the halogen atom gives way to another hydroxyl group, which, however, often enters partly in a position different from that occupied by the halogen. Under the further action of chlorine, tri- and penta-chlorophenol yield additive products, the C·OH group being at the same time converted into CO.

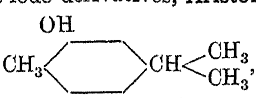
PHENOLSULPHONIC ACIDS, $OH \cdot C_6H_4 \cdot SO_3H$, are obtained by treating phenol with concentrated sulphuric acid, the o- and p-compounds being formed with equal ease ; the o- is converted into the p-compound by heating with water. The m-compound is obtained indirectly by fusing m-benzenedisulphonic acid with alkali.

HOMOLOGUES OF PHENOL (*see* Table, p. 540). Oxidation of the side-chains in these leads to aromatic hydroxy-acids.

The **Cresols** are not oxidised by chromic acid mixture, but are completely decomposed by permanganate ; if, however, the hydroxylic hydrogen is replaced by an alkyl or by acetyl, oxidation proceeds in the ordinary way.

The three isomeric **Hydroxytoluenes,** $CH_3 \cdot C_6H_4 \cdot OH$, bear the generic name of *cresols.* They are present in wood-tar and may also be prepared from the corresponding amino-derivatives or sulphonic acids. The cresols react with bromine water. The crude cresols mixed with soap solution form *creoline* or *lysol,* which serves as a convenient antiseptic and is largely used. **p-Cresol,** , is formed in the putrefaction of proteins.

THYMOL, , is found in oil of thyme and has an antiseptic action. One of its iodo-derivatives, **Aristol,** is used as a substitute for iodoform.

CARVACROL, , occurs in *Origanum hirtum,* and is formed by heating camphor with iodine or by the action of phosphoric acid on carvone (*see* Terpenes).

ANETHOLE, $CH_3O \cdot C_6H_4 \cdot CH : CH \cdot CH_3$, is a colourless solid melting at 228°, boiling at 233°, and having the sp. gr. 0·986 at 21·5° ; it has a pleasing odour and occurs in *Anise oil* (from the seeds of *Pimpinella anisum*), from which it is obtained by repeated fractional distillation or by freezing. Synthetically it is prepared from anisaldehyde and sodium propionate by Perkin's reaction (*see* p. 291), its constitution being thus proved. In the pure state it costs 20*s.* per kilo.

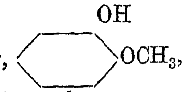
(*b*) DIHYDRIC PHENOLS

These contain two hydroxyl groups united to the carbon of the benzene nucleus. They are analogous in their chemical behaviour to monohydric phenols, and are prepared by similar methods ; certain of them show marked reducing properties. With lead acetate, pyrocatechol gives a white precipitate, hydroquinone is precipitated in presence of ammonia, while resorcinol is not precipitated.

PYROCATECHOL (Catechol), $C_6H_4(OH)_2$ (1 : 2), forms crystals melting at 104° and subliming ; it dissolves readily in water, alcohol, or ether. It is found in various resins and

is obtained by distilling catechu (*Mimosa catechu*); it is now prepared by fusing o-phenol-sulphonic acid (*see* p. 543) with caustic potash.

Its alkaline solution is unstable, and is coloured first green and then black by the oxygen of the air; it reduces silver salts, and by ferric chloride is coloured green or violet if a little ammonia is present (*characteristic reaction of ortho-dihydroxy-compounds*). With bromine water it gives *tribromoresorcinol,* which melts at 118°, is soluble in water, and turns brown in the air.

Its monomethyl **Ether,** 

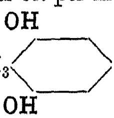
is called **GUAIACOL** and occurs abundantly in beech-tar; it is used in medicine as an expectorant. It is obtained by shaking the creosote oil (fraction boiling at 200° to 250°) from the distillation of the above tar with ammonia, treating with alcoholic potash, washing with ether, crystallising the potassium compound from alcohol, and decomposing it with dilute sulphuric acid. It is obtained crystalline by allowing its light petroleum solution to evaporate slowly. Synthetically it is prepared by diazotising o-anisidine, acidifying with dilute sulphuric acid, and distilling in steam. It melts at 29°, boils at 205°, and dissolves in about 60 parts of water. It costs from 10*s*. to 13*s*. per kilo.

RESORCINOL, $C_6H_4(OH)_2$ (1 : 3), is formed on fusing various resins, such as *galbanum* and *asafœtida,* with potash, and also from m-phenolsulphonic acid or m-bromobenzene-sulphonic acid; it is prepared industrially from m- or p-benzenedisulphonic acid (prepared from toluene-free benzene) by fusion with potash. It forms rhombic crystals melting at 110°, and boils at 270° with partial decomposition. It turns brown in the air, is soluble in water, alcohol, and ether, and slightly so in benzene, and reduces silver nitrate. It is a less energetic disinfectant than carbolic acid.

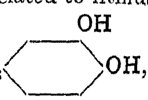
With nitrous acid or diazo-compounds it forms dyes and, like all m-dihydroxybenzenes, with phthalic anhydride at 200° it yields fluorescein. Commercial resorcinol costs 5*s*. 6*d*. per kilo and the pure compound 20*s*.

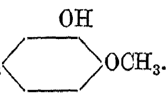
HYDROQUINONE (Quinol), $C_6H_4(OH)_2$ (1 : 4), is obtained by oxidising aniline in the *cold* with sulphuric and chromic acids, or by reducing quinone with sulphurous acid. It forms dimorphous crystals melting at 169°, and with ammonia gives a reddish brown coloration. Oxidising agents convert it into quinone. Owing to its strong reducing properties it is used as a photographic developer.

The chemically pure compound costs 8*s*. per kilo.

ORCINOL (Dihydroxytoluene), CH_3

, does not form fluorescein with phthalic anhydride. Its ammoniacal solution oxidises in the air, giving **Orceine,** $C_{28}H_{24}O_7N_2$, which is the principal component of natural *archil* and is related to litmus.

HOMOPYROCATECHOL (Homocatechol), CH_3

, gives a monomethyl ether, **Creosol,** CH_3

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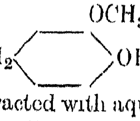
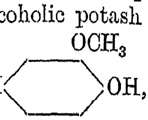
The unsaturated derivative, **Eugenol,** $CH_2 : CH \cdot CH_2$

, is the principal component (90 per cent.) of *clove oil,* from which it is extracted with aqueous potash, being then liberated with acid and rectified in a stream of CO_2. It is a liquid boiling at 247·5° and has the sp. gr. 1·073 at 14°. Hot alcoholic potash displaces the double linking of eugenol, giving **Isoeugenol,** $CH_3 \cdot CH : CH$

, which also has a pleasant, characteristic odour.

(c) TRIHYDRIC PHENOLS (Trihydroxybenzenes)

The constitutions of the three isomeric trihydroxybenzenes have now been fixed with certainty: Pyrogallol, 1 : 2 : 3; Hydroxyhydroquinone, 1 : 2 : 4 (*as*), and Phloroglucinol, 1 : 3 : 5 (*s*).

PYROGALLOL (1 : 2 : 3-Trihydroxybenzene; also improperly called Pyrogallic Acid), $C_6H_3(OH)_3$, is prepared by heating gallic acid (*see later*) for half an hour in an autoclave at 200° to 210° with 2 to 3 times its weight of water; the solution is decolorised by boiling with animal charcoal, filtered, concentrated, and crystallised. The pyrogallol thus obtained is purified by sublimation and then forms shining, white, poisonous scales or needles, melting at 132° and boiling at 210°. It may also be prepared by distilling a mixture of 1 part of gallic acid with 2 parts of powdered pumice in a current of CO_2.

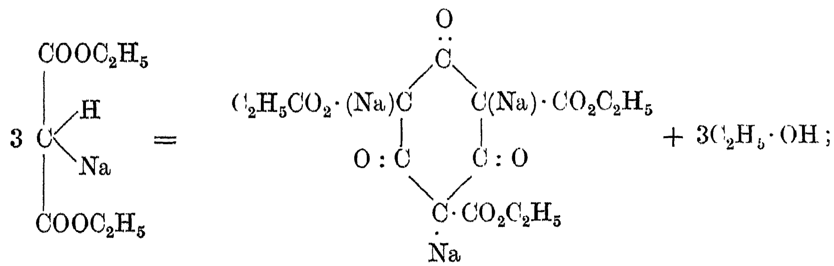
It dissolves in 1·7 part of water or ether, or in 1 part of alcohol. In alkaline solution it is an energetic reducing agent and absorbs oxygen from the air with avidity; it is used in gas analysis in all cases in which oxygen is to be absorbed (*see* Orsat Apparatus, vol. i, p. 375). By fresh solutions of ferrous sulphate it is coloured blue, by ferric chloride brown, and by silver nitrate black.

It does not react with hydroxylamine (*see* Phloroglucinol). Its dimethyl ether (Dimethyl Pyrogallate), $OH \cdot C_6H_3(OCH_3)_2$, is contained, along with other homologous ethers, in beech-tar.

When pure it costs 12*s*. to 14*s*. 6*d*. per kilo.

HYDROXYHYDROQUINONE (1 : 3 : 4-Trihydroxybenzene), $C_6H_3(OH)_3$, is obtained by fusing hydroquinone with caustic soda and has not been very closely studied. It crystallises from ether in plates melting at 140·5°, readily undergoes change in aqueous solution, and does not react with hydroxylamine (*see* Phloroglucinol).

PHLOROGLUCINOL, $C_6H_6O_3$, is obtained by fusing various resins with KOH. Baeyer prepared it synthetically by condensing 3 mols. of ethyl sodiomalonate in the hot, 3 mols. of alcohol being thus eliminated:



acidification of this product results in the substitution of the sodium by hydrogen with formation of *phloroglucinoltricarboxylic acid*, which, when fused with caustic potash, loses its carbethoxy-groups and gives phloroglucinol. The latter should therefore have the constitution $CO{<}\begin{smallmatrix}CH_2-CO\\CH_2-CO\end{smallmatrix}{>}CH_2$, which contains no double linking and corresponds with *triketohexamethylene*; in accord with this structure, it reacts with 3 mols. of hydroxylamine, giving a trioxime.

On the other hand, it behaves also as a trihydroxybenzene or trihydric phenol, giving a triacetyl-derivative with acetyl chloride, so that it is able to exist in two tautomeric forms.

This explains why, when it is treated with alcoholic potash or with an alkyl iodide, the alkyl groups unite with carbon and not with oxygen (as they would with a triphenol), giving, *e.g.* hexamethylphloroglucinol.

Pure phloroglucinol costs about £16 per kilo.

(*d*) POLYHYDRIC PHENOLS

From dinitroresorcinol is obtained a **Tetrahydroxybenzene,** $C_6H_2(OH)_4$ (1 : 2 : 4 : 5), which boils at 220°, while chloranilic acid (*see later*) is formed by the oxidation of the dichloro-derivative.

HEXAHYDROXYBENZENE, $C_6(OH)_6$, is obtained as potassium derivative, $C_6O_6K_6$, in the manufacture of potassium by reduction of its carbonate : $K_2CO_3 + C_2 = 3CO + K_2$ and $6K + 6CO = C_6O_6K_6$. These reactions represent a further example of the synthesis of organic substances from inorganic matter. Hexahydroxybenzene is a white, crystalline substance which oxidises readily in the air and yields benzene when distilled with zinc dust.

Of the additive products formed by polyhydric phenols with hydrogen, *quercitol* and *inositol* may be mentioned.

QUERCITOL (Pentahydroxycyclohexane or Acorn Sugar)

$$OH\cdot CH\langle\begin{matrix} CH(OH)\cdot CH(OH) \\ CH(OH)\cdot CH(OH) \end{matrix}\rangle CH_2,$$

s found in acorns and is similar to mannitol ; it has a sweet taste and forms monoclinic prisms melting at 234°, its specific rotation being $[\alpha]_D^{16} = +24{\cdot}16°$. When heated to 240° in a vacuum or fused with alkali it loses water yielding various aromatic derivatives (hydroquinone, quinone, and pyrogallol) ; on reduction with HI, it gives benzene, phenol, pyrogallol, quinone, and hexane. When oxidised with nitric acid it forms mucic and trihydroxyglutaric acids, while with permanganate it yields malonic acid, the presence of the methylene group, CH_2, being thus confirmed. It forms a pentacetyl-derivative, an explosive pentanitrate, and a pentachlorohydrin, $C_6H_7Cl_5$, melting at 102° ; the formation of these compounds demonstrates the presence of five hydroxyl groups.

INOSITOL (Hexahydroxycyclohexane or Muscle Sugar), $C_6H_6(OH)_6$, is similar to quercitol but contains a $CH\cdot OH$ group in place of the CH_2. It has the appearance and, to some extent, the sweet taste of the sugars, with which it was for long confused. That it is a cyclohexane derivative is shown by the formation of phenol, benzene, and triiodophenol on reduction with HI, and that of quinone and some of its derivatives on treatment with PCl_5. The presence of six hydroxyl groups is proved by the formation of a *hexa-acetate* (m.pt. 212°) when it is treated with acetic anhydride and zinc chloride, and of a *hexanitrate*, $C_6H_6(NO_3)_6$ (m.pt. 120°), under the action of concentrated sulphuric and nitric acids ; the hexanitrate is highly explosive and reduces Fehling's solution. Four optical isomerides are known: (1) inactive ; (2) dextro-rotatory, $[\alpha]_D + 68{\cdot}4°$, crystallising with $2H_2O$ and melting at 247° ; (3) lævo-rotatory, $[\alpha]_D - 65°$, m.pt. 247° ; (4) racemic, melting at 250°. Baeyer's stereochemical conceptions indicate eight possible isomerides, according to the arrangement of the OH and H above or below the plane of the hexagon. Inositol, especially the inactive form, occurs in beans, lentils, peas, the muscles of the heart, the brain, &c. The inactive modification crystallises from water with $2H_2O$ at temperatures below 50° and in an anhydrous form, m.p. 225°, at higher temperatures ; it boils unchanged in a vacuum at 319° and is not fermented by yeasts. It does not combine with phenylhydrazine or reduce Fehling's solution, but it reduces ammoniacal silver nitrate solution ; it forms a basic lead salt, $(C_6H_{11}O_6)_2Pb, PbO$. It does not yield quercitol when reduced, so that the hydroxyl groups are symmetrically distributed.

The monomethyl ether of i-inositol, or *bornesitol*, is found in Borneo rubber, and the dimethyl ether, or *dambonitol*, $C_6H_6(OH)_4(OCH_3)_2$, in Gabon rubber. The monomethyl ether of d-inositol, or *pinitol*, which occurs in many plants and plant-juices, melts at 186°, sublimes at 200°, and has a rotation of + 67·5°. The monomethyl ether of l-inositol, or *quebrachitol*, melts at 186°, boils at 200° *in vacuo*, and with HI forms l-inositol ; it occurs in quebracho bark.

E. QUINONES

These may be regarded as derivatives of phenols obtained by elimination of hydroxyl groups, with consequent displacement and partial elimination of the double linkings of the benzene nucleus. They are usually yellow and

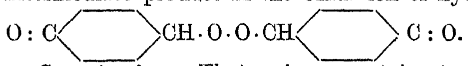
of pungent odour and possess oxidising properties ; they are volatile in steam, with partial decomposition.

Oxidation of meta- and ortho-diphenols does not yield quinones.

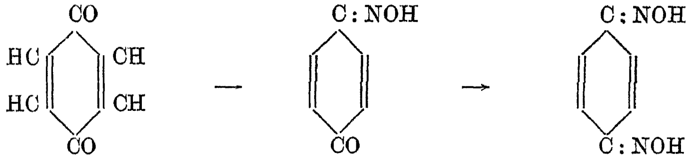
BENZOQUINONE or simply **Quinone**, $C_6H_4O_2$, can be obtained by oxidising either p-aminophenol or sulphanilic acid ($1:4 - NH_2 \cdot C_6H_4 \cdot SO_3H$), or p-phenolsulphonic acid, or hydroquinone, or aniline (on a large scale) with chromic acid.

On sublimation it forms fine yellow crystals which melt at 116°, giving a characteristic irritating odour. It is soluble in alcohol or ether and slightly so in cold water. It fixes hydrogen, which transforms it into hydroquinone, while the halogens give addition or substitution products according to the conditions. With HCl it forms monochlorohydroquinone, $C_6H_4O_2 + HCl = C_6H_3Cl(OH)_2$. With amines and with phenols it forms dyes which crystallise well but are only slightly soluble.

With hydroquinone it forms a condensation product, **Quinhydrone**, $C_6H_4O_2 \cdot C_6H_4(OH)_2$, which consists of green prisms with a metallic lustre, and may be regarded as an intermediate product in the oxidation of hydroquinone or in the reduction of quinone

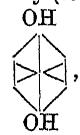
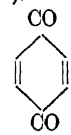


Constitution. That *quinone* contains two carbonyl groups is deduced from the fact that with hydroxylamine it yields *quinone monoxime* and *quinonedioxime* :



Quinonemonoxime (nitrosophenol)

It contains two double linkages, since in benzene solution it absorbs four atoms of bromine, while ozone is also fixed quantitatively (*see* pp. 88 and 299).

The transformation of hydroquinone, , into quinone, , is an evident example of the convertibility of the centric form of benzene into that with two double linkages.

Tetrachloroquinone (*chloranil*), $C_6Cl_4O_2$, prepared by oxidising trichlorophenol with dichromate and sulphuric acid, serves for the manufacture of coal-tar dyes ; the commercial product costs 20*s*. per kilo, and the pure 80*s*. *Toluquinone*, $C_6H_3O_2 \cdot CH_3$, *xyloquinone*, *thymoquinone*, &c., are known, as also are *quinoneimides* (*e.g.* $C_6H_4O \cdot NH$) and *quinonediimides* [*e.g.* $C_6H_4(NH)_2$].

F. NITRO-DERIVATIVES OF AROMATIC HYDROCARBONS

These are readily obtained by treating the hydrocarbons with concentrated nitric acid, best in presence of concentrated sulphuric acid, which fixes the water as it is formed :

$$C_6H_6 + HNO_3 = H_2O + C_6H_5 \cdot NO_2.$$

With the hydrocarbons homologous with benzene, nitration is still more easy, but not more than three nitro-groups can be introduced directly ; tetranitro-derivatives are prepared indirectly. Aromatic nitro-compounds cannot be obtained by the action of silver nitrite on chlorobenzenes, as is the case with those of the fatty series ; but this method serves for the introduction of nitro-groups into side-chains.

The nitro-compounds are liquid or solid and usually more or less yellow, although some are red ; they are heavier than water and dissolve readily in

MORE IMPORTANT NITRO-DERIVATIVES

Formula	Name	Positions of groups		Melting-point	Boiling-point	Specific gravity
		Alkyl	Nitro			
$C_6H_5 \cdot NO_2$	Nitrobenzene	—	1	+ 3°	208°	1·204 at 20°
$C_6H_4(NO_2)_2$	o-Dinitrobenzene	—	1 : 2	117°	319°	—
,,	m- ,,	—	1 : 3	90°	302°	1·369 at 98°
,,	p- ,,	—	1 : 4	172°	299°	—
$C_6H_3(NO_2)_3$	sym. Trinitrobenzene	—	1 : 3 : 5	122°	—	—
,,	as. ,,	—	1 : 2 : 4	57·5°	—	—
$C_6H_4(CH_3)(NO_2)$	o-Nitrotoluene (methylnitrobenzene)	1	2	− 10·5°	218°	1·168 at 15°
,,	m- ,, ,,	1	3	+ 16°	230°	1·168 at 22°
,,	p- ,, ,,	1	4	51°	234°	1·123 at 54°
$C_6H_3(CH_3)(NO_2)_2$	Dinitrotoluene (methyldinitrobenzene)	1	2 : 4	70°	—	1·321 at 70°
$C_6H_3(CH_3)_2(NO_2)$	Nitro-o-xylene (dimethylnitrobenzene)	1 : 2	4	29°	258°	1·139 at 30°
,,	,, -m- ,, ,,	1 : 3	4	2°	246°	1·135 at 15°
,,	,, -p- ,, ,,	1 : 4	2	liquid	240°	1·132 at 15°
$C_6H_2(CH_3)_2(NO_2)_2$	Dinitro-m-xylene (dimethyldinitrobenzene)	1 : 3	2 : 4	82°	—	—
,,	,, -m- ,, ,,	1 : 3	4 : 6	93°	—	—
$C_6H(CH_3)_2(NO_2)_3$	Trinitro-m-xylene (dimethyltrinitrobenzene)	1 : 3	2 : 4 : 6	182°	—	—
$C_6H_2(CH_3)_3(NO_2)$	Nitromesitylene (trimethylnitrobenzene)	1 : 3 : 5	2	44°	255°	—
$C_6H(CH_3)_3(NO_2)_2$	Dinitromesitylene (trimethyldinitrobenzene)	1 : 3 : 5	2 : 4	86°	—	—
$C_6(CH_3)_3(NO_2)_3$	Trinitrohemimellithene (trimethyltrinitrobenzene)	1 : 2 : 3	4 : 5 : 6	209°	—	—
,,	Trinitropseudocumene ,,	1 : 2 : 4	3 : 5 : 6	185°	—	—
,,	Trinitromesitylene ,,	1 : 3 : 5	2 : 4 : 6	231°	—	—
$C_6H(CH_3)_4(NO_2)$	Nitroprehnitene (tetramethylnitrobenzene)	1 : 2 : 3 : 4	5	61°	295°	—
$C_6H_3(CH_3)(C_3H_7)(NO_2)$	Nitrocymene (methylisopropylnitrobenzene)	1 : 4	2	liquid	—	1·085 at 15°
$C_6(CH_3)_4(NO_2)_2$	Dinitroprehnitene (tetramethyldinitrobenzene)	1 : 2 : 3 : 4	5 : 6	178°	—	—
,,	Dinitroisodurene ,,	1 : 2 : 3 : 5	4 : 6	156°	—	—
,,	Dinitrodurene ,,	1 : 2 : 4 : 5	3 : 6	205°	—	—
$C_6H(CH_3)(C_4H_9)(NO_2)_3$	Trinitro-tert. butyltoluene	1 : 3	2 : 4 : 6	97°	—	—

alcohol, ether, or acetic acid, but are mostly insoluble in water. They distil unchanged and are volatile in steam.

The nitro-group is united very firmly to the nucleus, especially in mononitrobenzene, and is not directly replaceable. It can be reduced to the *amino-group* by means of nascent hydrogen in *acid* solution ; reduction in alkaline solution results in the formation of azoxy-, azo-, and *hydrazo-compounds*, whilst in neutral solution or with hydrogen sulphide, the nitro-group becomes a hydroxyl-amino-group. On electrolytic reduction, nitro-derivatives yield amino-phenols.

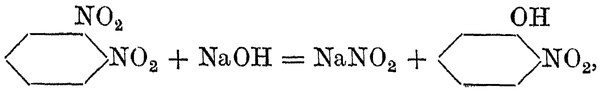
Polynitrobenzenes are easily obtained by the action of fuming nitric acid in the hot ; the **meta-derivative** is formed first and this, by further nitration with nitric and fuming sulphuric acids at 140°, gives symm. trinitrobenzene.

The polynitro-compounds react more readily than mononitro-derivatives ; when the former are oxidised, a phenolic group is formed, while the nitro-groups remain intact.

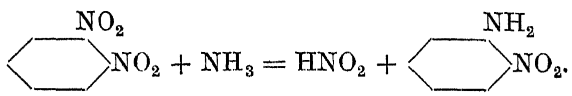
With para- and ortho-dinitrobenzenes, sodium alkoxide replaces one nitro-group quantitatively, whilst with m-dinitrobenzene no reaction occurs :

$$C_6H_4(NO_2)_2 + C_2H_5\cdot ONa = NaNO_2 + NO_2\cdot C_6H_4\cdot OC_2H_5.$$

By boiling o-dinitrobenzene with caustic soda, o-nitrophenol is formed :



while boiling with alcoholic ammonia yields o-nitralinine :



NITROBENZENE, $C_6H_5\cdot NO_2$, is an almost colourless, faintly yellow, refractive liquid which has the sp. gr. 1·209 at 15° and, after solidification, melts at 3° and boils at 208°. Owing to its pleasant bitter-almond smell, it is used in perfumery under the name of artificial *essence of mirbane*, but its vapour is somewhat poisonous. It is insoluble in water, but it mixes in all proportions with alcohol, ether, or benzene.

It is of considerable industrial importance, as it forms the raw material for the manufacture of aniline, benzidine, quinoline, azobenzene, various explosives, &c.

On a large scale it is prepared in wrought- or cast-iron vessels, employing precautions and methods similar to those used in making nitroglycerine (*see* p. 225). The nitro-sulphuric mixture, consisting of 120 kilos of HNO_3 (42° Bé.) and 180 kilos of H_2SO_4 (66° Bé.), is poured gradually (in 8 hours) into 100 kilos of benzene. The mass is kept mixed by means of a stirrer, and during the first 5 to 6 hours is maintained at 25° by means of cold water circulating outside the apparatus. In the final phase of the reaction the temperature is raised by external steam to 70° to 90°, the heating being then stopped, while the stirring is continued for a further 6 hours. The mass is then forced by a suitable elevator into a tank with a conical base. The acid mixture gradually settles to the bottom, while the nitrobenzene floats ; the former is then drawn off through taps (*see* Nitroglycerine), and the nitrobenzene, after repeated washing with water, distilled in a current of steam from a vessel with a jacketed bottom heated with steam at 2 to 3 atmos. pressure. A second distillation yields moderately pure nitrobenzene. According to Ger. Pat. 221,787 of 1907, nitrobenzene can also be obtained by running benzene into a mixture of sulphuric acid and sodium nitrate at 70° to 90°. It is sold at 72*s*. to 104*s*. per quintal.

The imports of nitrobenzene into Italy are as follow : 11 quintals in 1906, 18 in 1907, 138 in 1908, and 182, of the value of £874, in 1910.

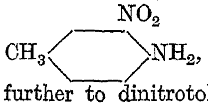
DINITROBENZENES. By the action of fuming nitric acid or of a suitable nitro-sulphuric mixture on benzene, m-dinitrobenzene is formed along with small proportions of the ortho- and para-compounds. The meta-derivative crystallises from alcohol in colourless needles, m.pt. 90°, and is insoluble in water, but readily soluble in alcohol or ether. The ortho- and para-isomerides are obtained indirectly from the corresponding dinitroanilines (*see* Aniline) by elimination of the amino-group ; both form colourless crystals. On reduction, m-dinitrobenzene gives first *m-nitraniline* and then *m-phenylene-diamine.* The crude product costs £6 per quintal, and the chemically pure 8*s.* per kilo. Dinitrobenzene dust is somewhat poisonous.

TRINITROBENZENE (symm.), $C_6H_3(NO_2)_3$. Attempts are now being made to utilise this compound as an explosive. It is obtained by oxidising trinitrotoluene (*see later*) with sulphuric and chromic acids (Ger. Pat. 127,325) and decomposing the resultant trinitro-benzoic acid by heat.

NITROTOLUENES

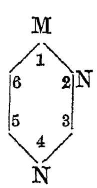
MONONITROTOLUENES, $NO_2 \cdot C_6H_4 \cdot CH_3$ (ortho-, m.pt. −10°, b.pt. 218° ; meta-, m.pt. + 16°, b.pt. 230° ; para-, m.pt. + 54°, b.pt. 236°). Large proportions of the ortho- and para-compounds and a small proportion of the meta-compound are obtained when toluene is nitrated with fuming nitric acid, the relative amounts varying with the conditions of the reaction. Thus, if highly concentrated nitric acid (sp. gr. 1·53) is employed and the mass is not cooled, 65 per cent. of p-nitrotoluene is obtained ; but if such a weak acid is used that it scarcely reacts, and the reacting mass is cooled, 67 per cent. of o-nitro-toluene is formed. When toluene is nitrated with nitric and sulphuric acids, 60 to 66 per cent. of the ortho-compound is obtained (100 kilos of toluene are added, in the course of 12 hours, to a mixture of 100 kilos of nitric acid of 44° Bé. with 150 kilos of sulphuric acid of 66° Bé., the mass being stirred and cooled and the decanted nitro-products washed with water and alkali) ; the unaltered toluene is distilled off in steam and the nitrotoluene eventually distilled by means of superheated steam. The ortho- and para-compounds are separated by fractional distillation ; 40 per cent. of ortho-compound distils at 222° to 223°, then a little meta-, and above 230° the *p-nitrotoluene.* The separation of the ortho- and para-isomerides may also be effected by cooling to − 6° (Ger. Pat. 158,219, Fr. Pat. 350,200), when almost colourless p-nitrotoluene (melting at 54° and boiling at 236° when pure) crystallises out ; *o-nitrotoluene* is a yellow liquid, which solidifies at − 10·5°, boils at 218°, and has the sp. gr. 1·168 at 15°. The crude mixture of these two isomerides costs 96*s.* to 112*s.* per quintal and is used, either as it is or after separation, for the manufacture of toluidine, tolidine, and fuchsine.

m-Nitrotoluene is formed in small quantity in the direct nitration of toluene (*see also* Dinitrotoluene), but in the pure state is obtained only indirectly from m-nitro-p-toluidine

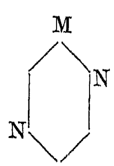


, by Griess's reaction (*see* Aniline). Only with difficulty is it nitrated further to dinitrotoluene, thus differing from the other mononitrotoluenes. It has no important practical use, and when impure costs 4*s.* per kilo, and when pure 32*s.* It forms crystals melting at 16°, boils at 230·5°, and has the sp. gr. 1·168 at 22°.

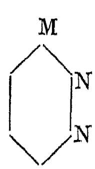
DINITROTOLUENES, $C_6H_3(CH_3)(NO_2)_2$, exist in six isomeric forms, which are prepared and named in various ways. Denoting the methyl group by M (always in position 1) and the nitro-group by N, the isomerides have the following configurations :



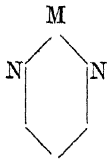
m-dinitrotoluene
ordinary dinitrotoluene
o : p-dinitrotoluene
α-dinitrotoluene
2 : 4-dinitrotoluene
m.pt. 70·5°



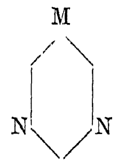
p-dinitrotoluene
ε-p-dinitrotoluene
2 : 5-dinitrotoluene
m.pt. 48°



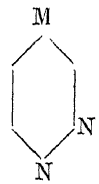
o : m-dinitrotoluene
1 : 2 : 3-dinitrotoluene
m.pt. 63°



o : o-dinitrotoluene
β-dinitrotoluene
2 : 6-dinitrotoluene
m pt. 61°



m . m-dinitrotoluene
δ-dinitrotoluene
3 : 5-dinitrotoluene
m.pt. 92°



m . p-dinitrotoluene
γ-dinitrotoluene
3 : 4-dinitrotoluene
m.pt. 60°

Of the various names, the last given in each case is the simplest and clearest.

When toluene is nitrated directly with a suitable nitro-sulphuric mixture (richer in nitric acid and poorer in water than for mononitrotoluene) and the mass is finally heated almost to boiling, the main product is ordinary solid dinitrotoluene (2 : 4), a little trinitrotoluene and 2 : 5-dinitrotoluene being also formed. About 35 per cent. of the crude mass always consists of a liquid product which is separated by centrifugation and was thought to be another isomeride, but Claus, Becker, Nölting, and Witt have shown it to be a mixture of 2 : 4- and 2 : 6-dinitrotoluenes and 40 per cent. of mononitrotoluenes (equal parts of p- and m- and a little o-); the mononitrotoluenes can be removed by distillation in a vigorous current of superheated steam. This orange-red mixture of liquid products gelatinises collodion-cotton well and serves for the preparation of *incongealable dynamites* and powders or dynamites with ammonium nitrate as basis.

2 : 4-Dinitrotoluene is prepared as described above and is the one in most common industrial use, while it serves also for making ordinary (2 : 4 : 6) trinitrotoluene. It is purified by crystallisation from alcohol or carbon disulphide and forms monoclinic crystals melting at 70·5° ; it is insoluble in water, slightly soluble in cold alcohol or ether, still less so in carbon disulphide (2·2 per cent.), and readily soluble in benzene. It dissolves in alkali, giving a red solution, from which acids precipitate a reddish brown substance. Fuming nitric acid oxidises it slowly and in the hot gives the corresponding *o : p-dinitrobenzoic acid*, $C_6H_3(CO_2H)(NO_2)_2$. With hot, concentrated nitro-sulphuric mixture, it forms ordinary trinitrotoluene (*see below*). Ammonium sulphide reduces it in the cold to *o-nitro-p-toluidine* (m.pt. 105°), while in the hot, *p-nitro-o-toluidine* (m.pt. 78°) is also formed. By zinc and hydrochloric acid it is reduced to *tolylenediamine*.

2 : 6-Dinitrotoluene is obtained along with the 2 : 4-isomeride and accumulates in the mother-liquors, when mononitrotoluene (ortho) is nitrated further. It is prepared in the pure state by eliminating the amino-group from dinitro-p-toluidine (m.pt. 168°). It forms shining needles, m.pt. 61°, dissolves to some extent in alcohol, and with ammonium sulphide gives o-nitro-o-toluidine.

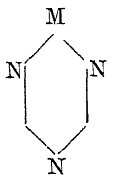
2 : 3-Dinitrotoluene is obtained by heating o : m-dinitro-p-toluic acid with dilute hydrochloric acid for 6 hours at 265° and distilling in a current of steam, the crystals formed being pressed or centrifuged ; it separates from light petroleum solution in yellow crystals, m.pt. 63°.

2 : 5-Dinitrotoluene is obtained together with the 2 : 4-derivative when toluene or nitrotoluene is run into fuming nitric acid ; it crystallises from alcohol in yellow needles, m.pt. 48°. Alcoholic ammonium sulphide reduces it to o-nitro-m-toluidine.

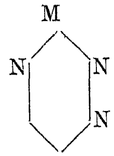
3 : 5-Dinitrotoluene is formed by eliminating the amino-group by diazotisation (*see* Aniline) from dinitro-o-toluidine (m.pt. 208°) or from m : m-dinitro-p-toluidine (m.pt. 168°). From water, in which it is sparingly soluble, it crystallises in needles, m.pt. 92°. It is soluble slightly in light petroleum, more so in cold alcohol or in carbon disulphide, and readily in chloroform, ether, or benzene. It distils easily in a current of steam, and with benzene forms the crystalline double compound, $C_6H_3(CH_3)(NO_2)_2 + C_6H_6$.

3 : 4-Dinitrotoluene is obtained by protracted agitation of m-nitrotoluene with concentrated nitric acid (sp. gr. 1·54). From carbon disulphide (which dissolves 2·19 per cent.), it crystallises in long needles melting at 60°.

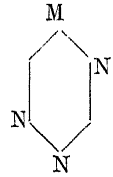
TRINITROTOLUENES. The following six isomerides are possible, only the first three being known :



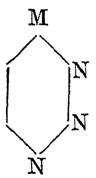
α-trinitrotoluene
2 : 4 . 6-trinitrotoluene
melts at 82° and solidifies
at 80·5



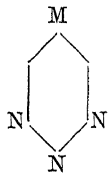
β-trinitrotoluene
2 . 3 : 6-trinitrotoluene
m pt 112°



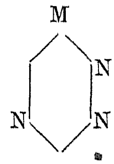
γ-trinitrotoluene
2 : 4 5-trinitrotoluene
m pt. 104°



2 . 3 : 4-trinitrotoluene



3 : 4 . 5-trinitrotoluene



2 : 3 : 5-trinitrotoluene

Rudeloff (1907) is of opinion that, together with α-trinitrotoluene, two other isomerides, melting at 73° and 78°, are formed, but these are probably more or less impure α-compounds.

α-TRINITROTOLUENE (*ordinary* or 2 : 4 : 6-Trinitrotoluene) is formed on heating toluene for several days or, better, 2 : 4-dinitrotoluene for some hours, with a highly concentrated nitro-sulphuric mixture, the operation being begun at a low temperature and with constant mixing, and the temperature being raised gradually to 100°. After removal of the acids by decantation, the mass is washed with boiling water and purified by crystallisation from alcohol or from concentrated sulphuric acid, in which it dissolves in the hot (V. Vender, Fr. Pat. 405,812 of 1909).

It forms pale yellow crystals which darken under the influence of light ; it melts at 82° and solidifies at 80·5°. At a higher temperature it undergoes partial sublimation, and when heated rapidly to 240° it sometimes explodes. It is very slightly soluble in water (0·164 per cent. at 100° and 0·021 per cent. at 15°) ; the mixture of nitric and sulphuric acids containing 15 per cent. of water dissolves from 2 per cent. to 5 per cent. according to the proportion of nitric acid present ; 99 per cent. sulphuric acid dissolves it to the extent of 66 per cent. at 100° and of 10 to 12 per cent. at 20°. Alcohol dissolves 2 to 3 per cent. of it in the cold and 25 per cent. in the hot ; it is readily soluble in ether, acetone, or benzene ; cold carbon disulphide dissolves only 0·39 per cent.

When non-compressed the crystals have the density 0·8 to 1, but if they are fused and allowed to solidify under ordinary pressure the density is 1·54 to 1·57 ; while if the solidification takes place under a pressure of 3 to 4 atmos. (Bichel, 1906) or with rapid cooling (Nobel Dynamite Co., Hamburg, 1907), the value 1·61 to 1·62 is attained. When the crystals are compressed in a hydraulic press to 200 to 600 kilos (or to 3000 kilos) per square centimetre, they assume a density of 1·59 (or 1·68).

When aniline is poured into an alcoholic solution of trinitrotoluene, a double compound, $C_6H_2(CH_3)(NO_2)_3 + C_6H_5 \cdot NH_2$, separates in red acicular crystals melting at 84°. If heated at 180° with ten times its weight of fuming nitric acid, trinitrotoluene is converted into s-trinitrobenzene. While picric acid (which is now partly replaced by trinitrotoluene as an explosive) readily forms with metals picrates dangerous to handle, trinitrotoluene does not react with metals and can be manipulated safely even in the hot, since it burns slowly without exploding ; it is not hygroscopic and does not form a bitter and poisonous powder like picric acid. It is highly stable to shock, and when compressed is exploded with a mercury fulminate cap ; but when fused and then solidified it is exploded only by a detonator of moderately compressed, crystalline trinitrotoluene, which in its turn is exploded by a fulminate cap. The *velocity of detonation* in a charge 50 mm. in diameter and with a density of 1·55 is 7500 metres (picric acid, 8000 metres).

The theoretical decomposition is expressed by: $2C_6H_2(CH_3)(NO_2)_3 = 12CO + 2CH_4 + H_2 + 3N_2$, 1 kilo giving 778 litres of gases, which are incompletely burnt owing to lack of oxygen.

The use of trinitrotoluene as an explosive was suggested prior to 1890, and attempts

were made to compensate the deficiency of oxygen by addition of ammonium nitrate. But it has been largely used, mainly as a result of Bichel's investigations, only since 1904, and in the crystalline state it now forms a very important military explosive. In the compressed or solidified state it is used for charging projectiles, grenades, &c (it does not serve for propelling projectiles, owing to its shattering power and to the abundance of fumes it forms on explosion). Different firms produce it under various names (*trotyl, trolite, trilite, trinol, tritole*). Germany manufactures 12,000 to 15,000 quintals per annum, and Italy 4000 to 5000; the price varies from 2*s.* 6*d.* to 4*s.* per kilo, according as it is crystallised, granulated, fused, or compressed.

For some time a plastic product called *plastrotyl* (Bichel, 1906) was prepared from trinitrotoluene, resin, collodion-cotton, and crude liquid dinitrotoluene, but this is no longer manufactured.

β-TRINITROTOLUENE or **2 : 3 : 6-Trinitrotoluene** is formed in small proportion with a large proportion of the γ-isomeride (*see below*) when m-nitrotoluene is boiled for a day with nitric and sulphuric acids. It separates from carbon disulphide or alcohol in colourless crystals melting at 112°, and is readily soluble in ether, acetone, or benzene. With alcoholic ammonia in the hot it gives γ-dinitrotoluidine (m.pt. 94°).

γ-TRINITROTOLUENE or **2 : 4 : 5-Trinitrotoluene** is formed with the β-isomeride (*see above*), from which it can be separated in virtue of its slight solubility in alcohol or carbon disulphide. It forms yellowish, shining crystals, melting at 104°. When heated with alcoholic ammonia it forms **β-Dinitrotoluidine**, while with aniline in the cold it gives **Phenyldinitrotoluidine**, melting at 193°. Also with aniline its hot alcoholic solution gives orange crystals of **γ-Dinitrotolylphenylamine**, m.pt. 142°.

CHLORO- and **BROMO-NITROBENZENES.** The para-derivatives melt at higher temperatures than the meta- and these at higher temperatures than the ortho-compounds. This rule often holds with aromatic compounds.

Nitration of chlorobenzene yields much *para-* and little *ortho*-derivative; the *meta*-compound is prepared indirectly from m-nitraniline by transforming the amino-group and replacing it by halogen.

TRINITROTERT.BUTYLXYLENE has an odour of musk and is used as a perfume.

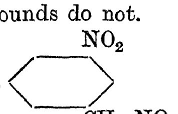
PHENYLNITROMETHANE, $C_6H_5 \cdot CH_2 \cdot NO_2$, contains the nitro-group in the side-chain, as is shown by its method of preparation:

$$\underset{\text{Benzyl chloride}}{C_6H_5 \cdot CH_2Cl} + AgNO_2 = AgCl + C_6H_5 \cdot CH_2 \cdot NO_2.$$

It is obtained also by heating toluene with nitric acid (sp. gr. 1·12) under pressure. This compound exists in two isomeric (or tautomeric) forms, one being known as a *pseudo-acid*: (1) $C_6H_5 \cdot CH_2 \cdot NO_2$ and (2) $C_6H_5 \cdot CH : NO \cdot OH$ (pseudo-acid); the former does not react with ferric chloride, while the latter gives a coloration. Modification (1) is a liquid, and its aqueous solution gives, with sodium alkoxide, the sodium salt of the pseudo-acid; when the acid is liberated by means of a mineral acid it forms a crystalline product, which has the same composition as the original compound and gradually changes into this, becoming liquid. The presence of a hydroxyl group in the pseudo-acid is demonstrated by the formation of the characteristic *dibenzhydroxamic* (or dibenzoylhydroxamic) acid by treatment with benzoyl chloride:

$$C_6H_5 \cdot CH : NO \cdot ONa + C_6H_5 \cdot CO \cdot Cl = NaCl + C_6H_5 \cdot CH : NO \cdot O \cdot CO \cdot C_6H_5$$
$$\longrightarrow \underset{\text{Dibenzhydroxamic acid}}{C_6H_5 \cdot CO \cdot NH \cdot O \cdot CO \cdot C_6H_5}$$

That these isonitro-compounds contain hydroxyl is shown also by the fact that they react in the cold with phenyl isocyanate, while the nitro-compounds do not.

Similar behaviour is shown by **m-Nitrophenylnitromethane**,  ; the passage from the yellow pseudo-acid to the colourless nitro-compound is clearly shown by the change both in colour and in electrical conductivity, which is very high for the pseudo-acid (as for acids in general) and almost zero for the normal nitro-compound, into which it is gradually converted.

These nitro-derivatives of the side chain can hence yield metallic derivatives—of the pseudo-acids ; treatment of these derivatives with acid yields the normal form, and the latter in presence of alkali is only *slowly* neutralised, this being characteristic of the *pseudo-acids*.

In benzene solution the true acids combine rapidly with ammonia, forming insoluble ammonium salts, while pseudo-acids combine only slowly or not at all with ammonia.

G. AMINO-DERIVATIVES OF AROMATIC HYDROCARBONS

When the hydrogen atoms of benzene are replaced by amino-groups or the hydrogen of ammonia or of a primary aliphatic amine by phenyl-groups, the resulting products are *mono-*, *di-*, or *tri-amines* in the first case and *secondary* and *tertiary amines* in the second.

Some of the aromatic amines are similar to but weaker than the aliphatic bases, the phenyl group being somewhat negative in character compared with the positive alkyl groups.

Aromatic amines form salts with acids and double salts with platinum chloride. In contact with the vapours of volatile inorganic acids they form white fumes in the air in the same way as ammonia ; they distil undecomposed. The diamines are more highly basic than the monamines.

Isomerides of the amines are formed when the amino group enters side chains.

1. PRIMARY MONAMINES

Primary, secondary, and tertiary aromatic monamines are distinguished by the same reactions as are used for aliphatic amines (by nitrous acid, &c. ; *see* p. 201).

Formation. (*a*) Mono-, di-amines, &c., are usually obtained by reducing the nitro-derivatives with tin or stannous chloride and hydrochloric acid, or with iron and acetic acid, or with ammonium sulphide, &c. : $C_6H_5{\cdot}NO_2 + 6H = 2H_2O + C_6H_5{\cdot}NH_2$. The reduction may also be effected electrolytically (*see later*, p. 566).

(*b*) By heating phenols (or, better, nitrophenols or naphthols) with ammoniacal zinc chloride at 300°, primary amines are readily obtained with small proportions of secondary amines : $C_6H_5{\cdot}OH + NH_3 = H_2O + C_6H_5{\cdot}NH_2$.

(*c*) By heating secondary and tertiary bases (substituted amines) with concentrated hydrochloric acid at 180°, $C_6H_5{\cdot}N(CH_3)_2 + 2HCl = C_6H_5{\cdot}NH_2 + 2CH_3Cl$; at higher temperatures the alkyl chloride reacts with the nucleus, giving homologous amines higher than the original one : $C_6H_5{\cdot}NH_2 + CH_3Cl = C_6H_4(CH_3){\cdot}NH_2, HCl$. In the same way, trimethylphenylammonium iodide yields mesidine hydriodide, $C_6H_2(CH_3)_3{\cdot}NH_2, HI$ (the methyl groups of the nucleus never assume the *meta*-position).

Properties. The primary monamines are liquid or solid and turn brown in the air. With acids they form crystalline salts soluble in water, but with carbonic acid they do not give salts, so that they may be liberated from their salts by means of sodium carbonate. With platinum chloride they form double salts (platinichlorides), *e.g.* $(C_6H_5{\cdot}NH_2, HCl)_2, PtCl_4$, which are only slightly soluble and serve for the separation of these bases.

With methyl iodide they form secondary, tertiary, and quaternary compounds : $C_6H_5{\cdot}NH{\cdot}CH_3, HI \rightarrow C_6H_5{\cdot}N(CH_3)_2, HI \rightarrow C_6H_5{\cdot}N(CH_3)_3I$; the base can easily be separated from the acid by caustic soda.

Benzaldehyde reacts with aniline, forming benzylideneaniline : $C_6H_5{\cdot}CHO + C_6H_5{\cdot}NH_2 = H_2O + C_6H_5{\cdot}CH:N{\cdot}C_6H_5$, while acetaldehyde gives ethylidenediphenyldiamine :

$$2C_6H_5{\cdot}NH_2 + CH_3{\cdot}CHO = H_2O + \begin{matrix}C_6H_5{\cdot}NH\\C_6H_5{\cdot}NH\end{matrix}\!\!>\!CH{\cdot}CH_3.$$

Aromatic Amines

Rational formula	Name	Melting-point	Boiling-point	Specific gravity
$C_6H_5 \cdot NH_2$	Aniline (aminobenzene)	– 8°	183°	1·024 at 16°
$CH_3 \cdot C_6H_4 \cdot NH_2$	o-Toluidine (1-methyl-2-aminobenzene)	liq.	199°	0·999 at 20°
„	m- „ (1- „ -3- „)	liq.	199°	0·998 at 25°
„	p- „ (1- „ -4- „)	42·8 °	198°	—
$(CH_3)_2C_6H_3 \cdot NH_2$	o-Xylidine (*vic.*) (1 : 2-dimethyl-3-aminobenzene)	liq.	223°	0·991 at 15°
„	o- „ (*as.*) (1 : 2- „ -4- „)	49°	226°	1·076 at 17°
„	m- „ (*vic.*) (1 : 3- „ -2- „)	liq.	215°	—
„	m- „ (*as.*) (1 : 3- „ -4- „)	liq.	215°	0·918 at 25°
„	m- „ (*s.*) (1 : 3- „ -5- „)	liq.	223°	0·972 at 15°
„	p- „ (1 : 4- „ -2- „)	15·5°	215°	0·980 at 15°
$C_2H_5 \cdot C_6H_4 \cdot NH_2$	p-Aminoethylbenzene (1-ethyl-4-aminobenzene)	– 5°	214°	0·975 at 22°
$(CH_3)_3C_6H_2 \cdot NH_2$	Mesidine (1 : 3 : 5-trimethyl-2-aminobenzene)	liq.	233°	—
„	Pseudocumidine (1 : 2 : 4-trimethyl-5-aminobenzene)	68°	234°	—
$(C_2H_5 \cdot CH_2) \cdot C_6H_4 \cdot NH_2$	p-Aminopropylbenzene (1-propyl-4-aminobenzene)	liq.	225°	—
$(CH_3)_2CH \cdot C_6H_4 \cdot NH_2$	Cumidine (1-isopropyl-4-aminobenzene)	liq.	218°	—
$(CH_3)_4C_6H \cdot NH_2$	Prehnidine (1 : 2 : 3 : 4-tetramethyl-5-aminobenzene)	70°	260°	—
„	Isoduridine (1 : 2 : 3 : 5- „ -4- „)	24°	255°	0·978 at 24°
$(CH_3)(C_3H_7)C_6H_3 \cdot NH_2$	Carvacrylamine (1-methyl-4-propyl-2-aminobenzene)	liq.	241°	0·944 at 24°
„	Thymenamine (1- „ -4- „ -3- „)	liq.	230°	—
$(CH_3)_2CH \cdot CH_2 \cdot C_6H_4 \cdot NH_2$	p-Aminoisobutylbenzene (1-γ-methylpropyl-4-aminobenzene)	17°	230°	0·937 at 25°
$(CH_3)_5C_6 \cdot NH_2$	Aminopentamethylbenzene (pentamethylaminobenzene)	152°	278°	—
$C_5H_{11} \cdot C_6H_4 \cdot NH_2$	p-Aminoisoamylbenzene	liq.	260°	—
$C_8H_{17} \cdot C_6H_4 \cdot NH_2$	p-Aminooctylbenzene (1-octyl-4-aminobenzene)	19·5°	310°	—
$C_{16}H_{33} \cdot C_6H_4 \cdot NH_2$	Aminocetylbenzene (hexadecylaminobenzene)	53°	255 (14 mm.)	—
$C_{18}H_{37} \cdot C_6H_4 \cdot NH_2$	Aminooctodecylbenzene (octodecylaminobenzene)	61°	274 (15 mm.)	—
$C_6H_4(NH_2)_2$	o-Phenylenediamine (1 : 2-diaminobenzene)	102°	252°	—
„	m- „ (1 : 3- „)	63°	287°	—
„	p- „ (1 : 4- „)	147°	267°	—
$CH_3 \cdot C_6H_4(NH_2)_2$	Tolylenediamine (1-methyl-2 : 3-diaminobenzene)	61°	255°	—
„	„ (1- „ -2 : 4- „)	99°	280°	—
„	„ (four other isomerides)	—	—	—
$C_6H_3(NH_2)_3$	Triaminobenzenes	—	—	—

The action of the organic acids on amines gives *acianilides*, which are decomposable by alkali :

$$C_6H_5\cdot NH_2 + CH_3\cdot COOH = H_2O + \underset{\text{Acetanilide}}{C_6H_5\cdot NH\cdot C_2H_3O}.$$

When heated with chloroform and alcoholic potash, the primary amines form isonitriles (*carbylamines*), which have most unpleasant odours. With carbon disulphide they give *thioureas*, which with P_2O_5 give mustard oils of the aromatic series.

With nitrous acid (or nitrites) in acid solution, amines yield *diazo-* or *diazoamino-compounds*, these giving phenols when boiled with water. Where the amino-group is in the side-chain, no diazo-derivative is formed.

Aniline, *see later*.

2. SECONDARY MONAMINES

These are basic in character, not when they are purely aromatic compounds, but only when they contain also aliphatic radicals. These mixed derivatives are obtained from primary amines by treatment with methyl iodide and, if the acetylated primary base is employed, the simultaneous formation of tertiary base is avoided : $C_6H_5\cdot NH\cdot COCH_3 + CH_3I = HI + C_6H_5\cdot N(CH_3)(COCH_3)$; the acetyl group may be removed by subsequent hydrolysis.

The secondary bases may be separated from the tertiary by means of nitrous acid (potassium nitrite), with which the former yield *nitrosamines* : $C_6H_5\cdot NH\cdot CH_3 + NO\cdot OH = H_2O + C_6H_5\cdot N(NO)\cdot CH_3$, which are neutral compounds, insoluble in water. When these nitrosamines are heated with hydrochloric acid (alcoholic), the NO group passes into the benzene nucleus : $C_6H_5\cdot N(NO)\cdot CH_3$ gives $C_6H_4(NO)\cdot NH\cdot CH_3$.

Pure aromatic secondary monamines are obtained by heating the primary bases with the corresponding hydrochlorides :

$$C_6H_5\cdot NH_2 + C_6H_5\cdot NH_2, HCl = (C_6H_5)_2NH + NH_4Cl.$$

3. TERTIARY MONAMINES

These are formed by alkylating primary or secondary bases.

Triphenylamine is obtained from bromobenzene by the action of dipotassio-aniline : $2C_6H_5Br + C_6H_5\cdot NK_2 = 2KBr + (C_6H_5)_3N$.

The purely aromatic tertiary monamines are not basic in character, and hence do not form salts. They do not give isonitriles with chloroform, or mustard oils with CS_2.

With alkyl iodides they form quaternary compounds. When they are treated with nitrous acid, the NO group enters the benzene nucleus, this reaction distinguishing these bases from the tertiary bases of the fatty series.

4. QUATERNARY BASES

These are analogous to the corresponding aliphatic compounds. Trimethyl-phenylammonium Hydroxide, $C_6H_5\cdot N(CH_3)_3OH$, for example, is strongly alkaline, colourless, and bitter, and is decomposed on heating.

5. DIAMINES, TRIAMINES, TETRAMINES, ETC.

These are obtained by reducing the corresponding nitroamino- or polynitro-derivatives ; thus Tetraminobenzene is formed from dinitro-m-diaminobenzene.

The polyamines give various reactions with nitroso-compounds of tertiary amines, with certain azo-dyes, &c.

The diamines and polyamines are solid substances, which distil unde-

composed and are soluble in hot water. They are colourless, but turn brown in the air with a rapidity increasing with the number of amino-groups; they give characteristic colorations with ferric chloride.

The ORTHODIAMINES form Anhydro-bases or Benziminazoles, *e.g.* $C_6H_4\langle{}^{NH}_{N}\rangle C\cdot CH_3$. Further, aldehydes react with the hydrochlorides of diamines, forming Anhydro-bases or Aldehydo-bases.

Glyoxals yield Quinoxaline, &c., while nitrous acid gives Azimino-compounds, *e.g.* Aziminobenzene (*aminoazophenylene*), $C_6H_4\langle{}^{NH}_{N}\rangle N$.

m-DIAMINES give, with nitrous acid, yellowish brown colouring-matters (*Bismarck brown:* sensitive reaction). With diazobenzene chloride they yield azo-dyes (*chrysoidin*). When oxidised together with p-diamines, they give a blue colour which becomes red on boiling.

p-DIAMINES, when oxidised with $MnO_2 + H_2SO_4$, yield quinone, $C_6H_4O_2$, and a homologue with a peculiar odour; some of them give colouring-matters when treated with solutions of hydrogen sulphide and ferric chloride.

ANILINE (Aminobenzene, Phenylamine), $C_6H_5\cdot NH_2$, was discovered in 1826 by Unverdorben among the products of the dry distillation of indigo and was called *crystalline*, since with acids it readily formed crystalline masses. It was then found also by Runge in 1834 in coal-tar, and he named it *kyanol* or *blue oil*, since with hypochlorite it gave a blue coloration and its salts a violet coloration.

In 1841 Fritsche obtained it by distilling indigo with potash, and he termed it, after the native name of the plant, "*anil*," *aniline*. In 1842 Zinin gave the name *benzidam* to the product obtained by reducing nitrobenzene with ammonium sulphide. The identity of these various substances and their true constitution was proved by Hofmann in 1843.

Industrially it is prepared by treating nitrobenzene with nascent hydrogen produced by the action of hydrochloric acid on iron filings or, better, turnings, as was proposed in 1864 by Béchamp, who first used acetic acid in place of hydrochloric:

$$C_6H_5\cdot NO_2 + 6HCl + 3Fe = C_6H_5\cdot NH_2 + 3FeCl_2 + 2H_2O.$$

The quantity of HCl consumed is, however, only one-fortieth of the theoretical amount, so that after a certain point the reduction is perhaps continued by the action of the iron on water in presence of ferrous chloride: $2Fe + C_6H_5\cdot NO_2 + 4H_2O = 2Fe(OH)_3 + C_6H_5\cdot NH_2$. The apparatus for manufacturing aniline consists of a cast-iron cylinder (the lower half is furnished with a discharge tap and is replaceable, as it corrodes rapidly) provided with a cover, through which pass a vertical stirrer worked by toothed wheels and a direct-steam coil. The cover is also fitted with a reflux condenser and a hopper with a wooden plug for the introduction of the iron turnings. A tube fixed laterally to the lower part of the reflux condenser carries off the aniline distilling with the steam to a condensing coil on one side. The operation is carried out as follows: 300 litres of water, 180 kilos of iron turnings, and 60 kilos of concentrated hydrochloric acid are kept stirred in the cylinder while 750 kilos of nitrobenzene are introduced. The reaction is started by a jet of direct steam, and is afterwards maintained by gradually adding moist iron turnings up to a total quantity of 650 kilos; these additions are made over a period of 6 to 7 hours and are arranged so that the mass is kept hot, but the reaction is allowed to calm down before fresh iron is introduced. If the reaction becomes violent, benzene and ammonia are formed instead of aniline. A further quantity of 100 to 150 kilos of iron turnings is added. The nitrobenzene evaporating with the water is condensed in the reflux condenser. At the end of the operation the vessel contains aniline, aniline hydrochloride, ferric oxide and o- and p-toluidines, together with a little unaltered nitrobenzene and some impurities such as azobenzene, &c. Thick milk of lime is then added until the reaction is strongly

alkaline, and the mass distilled with superheated direct steam. The condensed distillate separates into two layers, the lower one of aniline and the upper one of water containing 2 to 3 per cent. of aniline in suspension or solution ; this lower layer is used in the reduction of subsequent quantities of nitrobenzene. The decanted aniline is purified by distillation from an iron still. The decomposition of the aniline hydrochloride by milk of lime takes place according to the equation :

$$2C_6H_5\cdot NH_2, HCl + Ca(OH)_2 = CaCl_2 + 2H_2O + 2C_6H_5\cdot NH_2.$$

A purer product is obtained by rectification of the aniline in a vacuum apparatus.

It has also been proposed (Ger. Pat. 184,809) to reduce nitrobenzene by means of sodium bisulphite in the hot.

At one time the nitrobenzene employed was obtained from crude 90 per cent. benzene containing toluene, the resultant product being a mixture of aniline and toluidine, which served well for the preparation of certain dyes. But nowadays it is often regarded as preferable to start from pure benzene and pure toluene separately and to mix the aniline and toluidine subsequently in the required proportions.

Aniline can also be obtained by other processes which have not yet been applied on a large scale, *e.g.* by passing a mixture of nitrobenzene vapour with excess of hydrogen (or water-gas) over reduced copper turnings heated to 300° to 400° ; the copper acts as a catalyst and remains unchanged (Ger. Pat. 139,457). Some importance is now being assumed by the electrolytic process, according to which nitro-derivatives can be converted into amino-derivatives in presence of metallic salts (*e.g.* copper salts), which also separate at the cathode (*see* p. 566).

Aniline is a liquid which boils at 183° to 184°, has the sp. gr. 1·024 at 16°, and solidifies at − 8° (or − 20° if impure). It is colourless and refractive, but becomes brown in the air at a rate increasing with the proportion of impurities present. It is soluble in alcohol, ether, benzene, fatty oils and, to a slight extent (1 : 30) in water, and it dissolves sulphur (in the hot), phosphorus, camphor, indigo, a little water (in the hot), &c. ; it is readily oxidisable. It distils easily and completely in steam, and its vapour is somewhat poisonous [1] and combustible. As a base it is weaker than ammonia in the cold but stronger in the hot, but its aqueous solution does not react with litmus or turmeric paper. Although it is a weak base, it precipitates salts of zinc, aluminium, and iron, and in the hot it displaces ammonia from various salts.

With formaldehyde it gives a characteristic (for aniline and for the aldehyde) condensation product, $(C_6H_5\cdot N : CH_2)_3$, melting at 40°. With chloride of lime a solution of aniline becomes intensely blue if pure or violet if impure (sensitive reaction), the colour rapidly changing to brown ; if the aniline solution is very dilute this coloration does not appear, but a red colour will then form on further addition of a few drops of ammonium hydrosulphide, minimal traces (1 : 250,000) of aniline being thus detectable. Aniline or one of its salts forms p-aminobenzenesulphonic acid with concentrated sulphuric acid, but in presence of a drop of potassium dichromate solution a fine blue colour is produced which disappears very rapidly ; in dilute solution a green and then a black colour (aniline black) is formed. Different methods of oxidising aniline give varied products : azobenzene, nitroso- and nitro-benzene, β-phenylhydroxylamine, p-aminophenol, quinone, p-aminophenylamine, violaniline (with arsenic acid). Oxidation of a mixture of aniline and toluidine yields fuchsine, while a mixture of aniline and p-diamine gives safranine.[2] Chlorine transforms dry aniline into

[1] Aniline acts on the nervous system, and even when its action is slight the edges of the lips are turned bluish and an effect similar to drunkenness is produced, but the face becomes pale and the appetite fails ; in such cases Epsom salts are administered as purgative, alcoholic liquors being harmful. Clothes soaked in aniline may produce serious poisoning, the lips becoming dark blue or even black, and giddiness so acute as to cause collapse When this happens, recourse should be had to excitants or ablution or to small doses of ether administered internally. Benzene and nitrobenzene vapours are also injurious to health.

[2] For the making of aniline black and other dyes, the following qualities of aniline are placed on the market *aniline oil for blue*, which is almost pure aniline, b.pt. 182° to 186°, sp. gr. 1·034 to 1·036 ; *aniline oil for red*, consisting of about 1 part of aniline and 2 parts of o- and p-toluidines and boiling at 190° to 198° ; *aniline oil for safranine*, sp. gr. 1·032 to 1·034, containing 35 to 50 per cent. of aniline and 50 to 65 per cent. of o-toluidine Aniline oil is tested commercially by measuring the fractions distilling at different temperatures from 100 grms·

a tarry substance, while in presence of water trichloraniline and trichlorophenol are formed. The action of calcium hypochlorite on a solution of aniline in chloroform yields azobenzene.

In 1909 Germany imported 639 quintals of aniline and exported 78,835 quintals (70,452 in 1908). According to the official statistics, Italy imported the following quantities of aniline oil and salt: 426 quintals in 1908; 577 in 1909; 3695, of the value of £20,680, in 1910. But these figures are obviously inaccurate, and private information shows that the Italian consumption (nearly all imported) must exceed 8000 quintals per annum, one-half of this being aniline salt (hydrochloride) and the other oil. In 1911 England exported aniline and toluidine oils to the value of £39,814.

Chemically pure aniline costs 2*s.* to 4*s.* per kilo; aniline oil for blue and for black costs 104*s.* to 112*s.* per quintal, and that for red 120*s.* to 152*s.*; lower prices than these sometimes prevail. Aniline salt costs about 10*s.* less per quintal than the oil. There is no import duty on the oil or salt in Italy.

Some of the more important salts and derivatives of aniline and its homologues are as follow:

ANILINE HYDROCHLORIDE (Aniline Salt), $C_6H_5 \cdot NH_2$, HCl, is obtained pure and dry in white crystals by passing a current of dry hydrogen chloride into an ethereal solution of aniline. It melts at 198° and partly sublimes, and boils unchanged at 245°; it dissolves readily in water or alcohol, but is insoluble in ether. For price, *see above.*

It is prepared industrially by neutralising aniline at 100° with concentrated hydrochloric acid, free from chlorine. After standing for some days, crystalline aniline salt separates out, this being centrifuged and dried at 50°; the mother-liquors are then evaporated and crystallised. In the air the white scales assume a reddish or greenish tint. In presence of HCl its aqueous solution imparts a yellow colour to pine-wood or elder-pith.

ANILINE SULPHATE, $(C_6H_5 \cdot NH_2)_2$, H_2SO_4, is only slightly soluble in water.

Various other salts of organic and inorganic acids are known.

ANILINE PLATINICHLORIDE, $(C_6H_5 \cdot NH_2, HCl)_2$, $PtCl_4$, forms yellow leaflets dissolving readily in water and, to a less extent, in alcohol.

METHYLANILINE, $C_6H_5 \cdot NH \cdot CH_3$, is obtained by heating aniline hydrochloride with methyl alcohol (free from acetone) at 200° in an enamelled iron autoclave. It is a colourless liquid, sp. gr. 0·976 at 15°, b.pt. 191°, with an odour resembling, but stronger than, that of aniline. With chloride of lime it gives first a violet and then a brown coloration. The corresponding nitrosamine, $C_6H_5 \cdot NO \cdot CH_3$, is obtained by methylating phenylnitrosamine or by treating methylaniline with nitrous acid. It forms a yellow oil which distils unchanged only in a current of steam and gives Liebermann's reaction, characteristic of the nitrosamines and of various nitroso-derivatives; this reaction consists in the formation of a dark blue coloration when the nitroso-compound is heated with phenol and sulphuric acid and the liquid then diluted with water and neutralised with potash.

DIMETHYLANILINE, $C_6H_5 \cdot N(CH_3)_2$, is a mixed tertiary amine and is obtained by heating aniline hydrochloride with methyl alcohol, methyl chloride being formed as an intermediate product and reacting with the aniline. If, however, dimethylaniline hydrochloride is heated with gaseous hydrogen chloride at 180°, methyl chloride and aniline are formed. When dimethylaniline is heated to a high temperature, the alkyl groups pass into the nucleus. The hydrogen in the para-position of these dialkylamines is readily replaceable by different groups; thus, the action of nitrous acid yields *p-nitrosodimethylaniline,* which forms green crystals and gives a yellow hydrochloride. Permanganate converts the NO group into NO_2, giving *nitrodimethylaniline* (m.pt. 162°), while boiling with caustic soda results in the elimination of dimethylamine and the formation of *nitrosophenol,* $NO \cdot C_6H_4 \cdot OH$. It gives a straw-yellow coloration with chloride of lime and reacts with aldehydes and various other compounds.

DIPHENYLAMINE, $C_6H_5 \cdot NH \cdot C_6H_5$, is obtained by heating aniline with its hydrochloride:

$$C_6H_5 \cdot NH_2, HCl + C_6H_5 \cdot NH_2 = NH_4Cl + C_6H_5 \cdot NH \cdot C_6H_5.$$

of the oil in a suitable distilling flask fitted with a thermometer graduated in fifths of a degree from 150° to 225° the heating being carried out on a sand-bath. The best qualities of aniline oil give 95 to 98 per cent of distillate between 182° and 185°. It is also advisable to make small dyeing tests with aniline black in order to ascertain which of the different aniline oils and salts on the market gives the finest and most intense black (*see later,* Dyeing Processes).

It melts at 54° and boils at 310°, and forms a very sensitive reagent for the detection of traces of nitric acid, with which, in presence of concentrated sulphuric acid, it gives an intense blue coloration (also given with nitrous acid and various oxidising agents; *see* Detection of Nitrates in Water, vol. i, p. 214).

Various nitro- and nitroso-derivatives are known, as well as *triphenylamine*, $N(C_6H_5)_3$, which crystallises in large plates melting at 127° and distils unchanged.

BENZYLANILINE (Benzylphenylamine), $C_6H_5 \cdot CH_2 \cdot NH \cdot C_6H_5$, is obtained either by heating benzyl chloride (1 mol.) with aniline (2 mols.) or by reducing *thiobenzanilide*, $C_6H_5 \cdot CS \cdot NH \cdot C_6H_5$. It forms crystals melting at 33° and boils at 310°.

ANILIDES are derivatives of aniline in which one or both of the hydrogen atoms of the amino-group of aniline are replaced by one or two inorganic or organic acid residues; in the latter case, compounds of considerable interest are formed.

ACETANILIDE (Antifebrin), $C_6H_5 \cdot NH \cdot COCH_3$, is obtained by boiling a mixture of aniline and glacial acetic acid for a couple of days in an earthenware vessel fitted with a reflux condenser:

$$C_6H_5 \cdot NH_2 + CH_3 \cdot CO \cdot OH = H_2O + C_6H_5 \cdot NH \cdot COCH_3.$$

It is purified by repeatedly crystallising or distilling, best *in vacuo*. It melts at 113°, boils at 295°, and dissolves in 174 parts of cold or 18 parts of boiling water or in $3\frac{1}{2}$ parts of alcohol; it is readily soluble in ether or chloroform. The hydrogen atom united to nitrogen can be replaced by metals (Na, K, &c.). It causes considerable lowering of the temperature of animal organisms, and is hence used as an antipyretic. It costs about 2*s.* 6*d.* per kilo.

Di- and **Tri-acetanilides** have analogous properties, and **Methylacetanilide**, $C_6H_5 \cdot N(CH_3) \cdot COCH_3$, is used under the name of *exalgin* as a specific against headache.

PHENYLSULPHAMINIC ACID, $C_6H_5 \cdot NH \cdot SO_3H$, is obtained by the action of sulphur trioxide on the amine, and is very unstable except in the form of salts.

CHLORACETANILIDE, $C_6H_4Cl \cdot NH \cdot COCH_3$, exists in three isomeric forms: the ortho-compound, melting at 88°; the meta-, at 72·5°; and the para-, at 172°. The chloro- and bromo-derivatives of acetanilide and other anilides are obtained by the action of chlorine or bromine on the anilide or by the interaction of acetyl chloride and the substituted anilines. Another series of isomerides is that in which the substitution is in the acid group, *e.g.* **Phenylchloracetamide**, $C_6H_5 \cdot NH \cdot CO \cdot CH_2Cl$ (m.pt. 134°), which is obtained from chloracetyl chloride and aniline. Phenyldichlor- (m.pt. 118°) and phenyltrichlor-acetamide (m.pt. 82°) are also known.

NITRACETANILIDE, $NO_2 \cdot C_6H_4 \cdot NH \cdot COCH_3$. The three isomerides are obtained by the action of acetyl chloride on the corresponding nitranilines; the o-compound melts at 92° (yellowish crystals), the m- at 142°, and the p- at 207°.

PHENYLACETANILIDE (Diphenylacetamide), $(C_6H_5)_2N \cdot CO \cdot CH_3$, is obtained by treating a benzene solution of diphenylamine with acetyl chloride; it melts at 99·5°.

BENZANILIDE (Phenylbenzamide), $C_6H_5 \cdot NH \cdot COC_6H_5$, is prepared from benzoyl chloride and aniline and melts at 162°. It is very stable, but is decomposed by fusion with alkali. It is insoluble in water, but dissolves in alcohol.

PHENYLGLYCOCOLL (Phenylaminoacetic or Anilidoacetic Acid), $C_6H_5 \cdot NH \cdot CH_2 \cdot CO_2H$, is obtained by protracted heating of chloroacetic acid (1 mol.) and aniline (2 mols.) with water. It forms crystals melting at 127°, gives characteristic mercury and copper salts, and when heated at 150° gives up water and yields the anhydride $C_6H_5 \cdot N\begin{cases} CH_2 \\ | \\ CO \end{cases}$, melting at 263°.

HOMOLOGUES OF ANILINE, POLYAMINES, AND THEIR DERIVATIVES

(*see* Table, p. 555)

ORTHO- and **PARA-TOLUIDINES**, $CH_3 \cdot C_6H_4 \cdot NH_2$, are obtained by reducing the corresponding nitro-compounds. Since the three isomerides are formed simultaneously in the nitration of toluene, reduction yields a mixture of the three toluidines (m-toluidine in small amount). In order to separate them, the mixture is poured into a solution of oxalic acid containing hydrochloric acid and the liquid heated to boiling; the p-toluidine oxalate, which is only slightly soluble in water and insoluble in ether, is then separated, the filtrate containing the soluble hydrochlorides of the other toluidines. Also Wülfing

has shown that only amines which have the para-position free can be converted (by HCl + $NaNO_2$) into the corresponding aminoazo-derivatives, the unaltered p-toluidine being then separable by distillation in steam. p-Toluidine can also be separated by cooling, since it freezes first. The toluidines are distinguished from aniline by the different solubilities of the nitrates, hydrochlorides, and acetyl-derivatives. p-Toluidine, like the meta-compound, costs double as much as the ortho-isomeride. *o-Toluidine*, which is also found in coal-tar, is a liquid (sp. gr. 1·09) boiling at 199° and turning brown in the air. *p-Toluidine* is a solid melting at 43°, and boils at 198° ; it is sparingly soluble in cold water, but dissolves readily in alcohol, ether, or benzene. The toluidines are used in the manufacture of dyes.

m-TOLUIDINE is obtained indirectly by nitrating acetylated p-toluidine, the compound CH_3  $NH\cdot COCH_3$ being thus formed ; the acetyl-group is then elimi-
NO_2
nated by boiling with hydrochloric acid and the amino-group by diazotisation. Reduction of the resultant m-nitrotoluene yields m-toluidine, which is a colourless oil (sp. gr. 0·998 at 25°) boiling at 197°. The crude product costs 4*s*. per kilo and the pure ten times as much.

XYLIDINES. Six isomerides are known (*see* Table, p. 555), and all are formed together by nitrating crude xylene and reducing the resulting nitro-compounds ; the most important is m-xylidine. Various methods of separating the different xylidines are known, almost all of them being patented and based on the varying solubilities of the acetates and hydrochlorides of p- and m-xylidines. The separate isomerides are prepared pure from the corresponding pure nitro-compounds.

BENZYLAMINE, $C_6H_5\cdot CH_2\cdot NH_2$, is isomeric with the toluidines and behaves like the amines of the aliphatic series. It is obtained together with di- and tri-benzylamine by heating benzyl chloride with ammonia. It is a colourless liquid of ammoniacal odour and boils at 185° ; it has an alkaline reaction and is a more energetic base than aniline, the amino-group being further removed from the benzene nucleus, which has a somewhat negative (acid) influence.

PHENYLENEDIAMINES, $C_6H_4(NH_2)_2$, are obtained by reducing the corresponding dinitrobenzenes or nitroanilines with iron and hydrochloric acid. *m*-Phenylenediamine is also obtained by electrolysing m-nitroaniline in aqueous saline solution in presence of a cathode of copper or of powdered copper (Ger. Pat. 131,404). It forms acicular crystals melting at 63°, boils at 287°, and readily undergoes change in the air ; its hydrochloride is, however, stable. It is used in the manufacture of dyes and also as a reagent for detecting traces of nitrous acid, with which it forms a brownish yellow coloration (Bismarck brown). *p*-Phenylenediamine is obtained by the reduction of aminoazobenzene (dissolved in aniline) with hydrogen sulphide, or, more easily, by heating p-dichlorobenzene or p-chloraniline with ammonia in presence of a copper salt (Ger. Pat. 204,408). It melts at 147°, boils at 267°, and forms crystals which are soluble in water and blacken a little in the air ; when pure it costs 40*s*. per kilo, the commercial product being sold at about 14*s*. As well as for making dyes, it is frequently employed for *dyeing hair* by oxidising it with hydrogen peroxide, but its use for this purpose should be prohibited owing to its poisonous properties (*see below*, p-Tolylenediamine). Its asymmetric dimethyl-derivative, $NH_2\cdot C_6H_4\cdot N(CH_3)_2$, is used in presence of ferric chloride to detect traces of hydrogen sulphide (*methylene blue* being formed).

o-Phenylenediamine is of no practical importance.

Commercial m-phenylenediamine costs about 6*s*. and its hydrochloride 7*s*. per kilo, the pure products costing about six times as much.

TOLYLENEDIAMINES, $C_6H_3(CH_3)(NH_2)_2$. The most common of these is the o : p-compound, *i.e.* the one with the amino-groups in the 2 and 4 positions and the methyl group in the position 1. It is obtained by reducing the corresponding dinitrotoluene (*see* p. 550) with iron and hydrochloric acid and is used for making dyes and, together with sodium sulphite, for dyeing hair, as it does not seem to be injurious to health, as p-phenylenediamine is. It costs about 16*s*. per kilo.

NITROANILINES. Concentrated nitric acid acts very energetically on aniline, and in order that the nitro-groups may be introduced into the benzene nucleus without the amino-group being attacked, either the amino-group is acetylated or the nitration is carried out in presence of a large proportion of

concentrated sulphuric acid. In the former case, ortho- and, to a still greater extent, para-**Nitroacetanilide**, $NO_2 \cdot C_6H_4 \cdot NH \cdot C_2H_3O$, are obtained, the acetyl group being then removed by hydrolysis with HCl or KOH; in the second case a mixture of m- and p-nitroanilines, together with a little of the ortho-compound, are obtained. The ortho- and meta-derivatives distil unchanged in steam. Boiling with alkali results in the elimination of the amino-groups and the formation of nitrophenols.

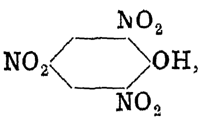
PICRAMIDE, $(NO_2)_3C_6H_2 \cdot NH_2$, is a yellow substance melting at 188°; on hydrolysis it gives picric acid.

H. NITROPHENOLS, AMINOPHENOLS

NITROPHENOLS. The ortho- and para-compounds are obtained mixed by treating phenol with dilute nitric acid, a larger proportion of the para-derivative being formed in the cold and of the ortho- in the hot. The latter is volatile in steam, and can hence be readily separated from the former.

m-Nitroaniline gives *m-nitrophenol* only by passing through the diazo-compound, but o- and p-nitroanilines give the corresponding nitrophenols when simply fused with potash.

Nitrophenols are more markedly acid than the phenols and decompose the alkali carbonates, forming **Nitrophenoxides**.

PICRIC ACID (Trinitrophenol).  was discovered in 1771 by Amato di Welter, but was first used as a dye and much later as an explosive. It is formed by the action of concentrated nitric acid on various substances, such as silk, wool, indigo, &c., and by the oxidation of s-trinitrobenzene with potassium ferricyanide. Further nitro-groups cannot be introduced directly into picric acid.

It is prepared industrially as follows: equal weights of sulphuric acid (66° Bé.) and pure phenol are heated at 120° in a cast-iron vessel and continually stirred until a small portion of the mass dissolves in water without separation of phenol. The phenolsulphonic acid thus obtained is poured into two parts of cold water and the solution introduced gradually into earthenware jars containing 65 per cent. nitric acid (sp. gr. 1·400) in the proportion of 3·5 parts per 1 part of phenol. The jars are surrounded by a water-bath and are covered over so that the nitrous fumes, which are at first freely evolved, may be drawn off. Towards the end of the reaction the water-bath is heated to boiling. The stages of the process are represented by the following equations:

$$(1)\ C_6H_5 \cdot OH + H_2SO_4 = H_2O + OH \cdot C_6H_4 \cdot SO_3H;$$

$$(2)\ OH \cdot C_6H_4 \cdot SO_3H + 3HNO_3 = 2H_2O + H_2SO_4 + OH \cdot C_6H_2(NO_2)_3.$$

When the mass is cool it solidifies, and it is then centrifuged and washed with a little water; by this means the picric acid crystals can be efficiently separated from the mother-liquor. The acid can also be prepared by the following process, the details of which are kept secret by the various manufacturers: To pure crystallised phenol (m.pt. 40°), fused in a number of pear-shaped retorts by means of indirect steam, is added a mixture of nitric and sulphuric acids in proportions varying in different works. When the reaction is finished, the clots of picric acid formed are fused and allowed to fall into a trough containing cold water, with which they are kept stirred, the water being repeatedly renewed until washing is complete. The crystallised picric acid is centrifuged, again melted and run into cold water, the size of the yellow scales separating out increasing with the temperature of the fused acid; the crystals are then centrifuged, spread out on tables, and dried in a current of air at 40° to 60°.

A suggestion has been made to prepare picric acid in the cold, as follows (Fr. Pat. 345,441): 1 part of crude phenol is stirred into a mixture of 10 parts of nitric acid (sp. gr. 1·4) with 3 parts of denatured alcohol, the mass being poured into hot water at the end of the reaction; the yield is good, but part of the alcohol is oxidised and lost. When phenol is dear, aniline is sometimes used, being converted into the sulphonic acid, diazotised, and treated with the theoretical quantity of nitric acid (Ger. Pat. 125,096).

Properties. Picric acid forms yellowish, very bitter, and somewhat poisonous leaflets, which melt at 122·5° and have the sp. gr. 1·7635 or, in the fused state, 1·62. It burns without exploding, but if it is heated in a closed vessel, or if its vapour is superheated, it may explode with great violence. In the open, mercury fulminate is not able to explode it, a detonator of dry guncotton (or lead picrate) with a mercury fulminate cap being necessary. When it is exploded in a closed vessel, its shattering effect is double that of dynamite.

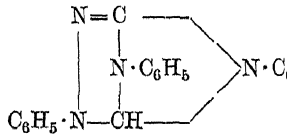
One hundred parts of water dissolve 0·626 part of picric acid at 5°, 1·161 part at 15°, 1·225 part at 20°, or 3·89 parts at 77°. It is readily soluble in alcohol, and benzene dissolves 8 to 10 per cent. of it at the ordinary temperature. In aqueous solution it is dissociated to some extent and shows a marked acid action. The yellow colour of its aqueous solution is due to the anion; in light petroleum it gives a colourless solution, and is hence non-ionised.

It is non-volatile in steam. Its hydroxyl-group is highly reactive, owing to the presence of the three nitro-groups. The potassium and ammonium salts are exploded by percussion, whilst the free acid requires a detonator.

With many aromatic hydrocarbons it forms well-crystallised, molecular compounds which serve for the identification and separation of the hydrocarbons; picric acid is eliminated from these compounds by ammonia.

With potassium cyanide it gives a characteristic and sensitive coloration (*isopurpuric acid*). With nitron acetate it gives a precipitate of nitron picronitrate, $C_{20}H_{16}N_4$, $C_6H_3O(NO_2)_3$, which is insoluble in extremely dilute aqueous solutions acidified with sulphuric acid, and can be filtered off, washed with water, dried at 110°, and weighed.

NITRON has the structure



, and in presence of acetic acid precipitates NO_3 ions from very dilute solutions even when nitrites are also present.

The decomposition of picric acid on explosion has not been thoroughly investigated, but is represented approximately by the equation:

$$C_6H_2(OH)(NO_2)_3 = 6CO + H_2O + 3N + H;$$

the acid is hence too poor in oxygen to give the maximum effect, the carbon monoxide and hydrogen not being oxidised.

Uses. Picric acid is employed in the preparation of certain organic compounds and was at one time used for dyeing silk and wool yellow, but the colour is not very stable. It is now mostly used as an explosive, either as acid or in the form of ammonium or potassium salt, these exploding at 310° or on percussion (*see* Explosives, pp. 215 *et seq.*). *Melinite*, a very powerful explosive suggested by Turpin for filling grenades, is merely picric acid which has been fused in a tinned vessel; it is poured into the empty grenade, the interior of which is also tinned.

From ammonium picrate and ammonium salts of trinitrocresol, sometimes with addition of potassium nitrate, powerful and stable explosives are obtained, these bearing various names (*lyddite, ecrasite,* &c.).

In 1905 Germany produced 10,350 quintals of picric acid (at £9 per quintal) for export alone.

AMINOPHENOLS, $NH_2 \cdot C_6H_4 \cdot OH$, are crystalline, colourless substances, which turn brown and resinify in the air. They are formed by reducing

nitrophenols and form salts only with acids. *p*-**Aminophenol**, melting at 183°, is obtained by electrolytic reduction of nitrobenzene in acid solution; it is stable in a solution of sodium sulphite and is used thus as a photographic developer under the name *rodinal*. Methyl-p-aminophenol, or *metol*, also serves as a developer.

Aromatic *photographic developers* (*see* vol. i, p. 800) should contain several hydroxyl- or amino-groups, or at least one group of each kind; if the hydrogen of the hydroxyl- and amino-groups is partly replaced, the compounds lose their developing properties, unless some of these groups remain unchanged.

AMINOANISOLES (Anisidines), $NH_2 \cdot C_6H_4 \cdot OCH_3$, and **Phenetidines**, $NH_2 \cdot C_6H_4 \cdot OC_2H_5$, are used in making azo-dyes and are similar to aniline. Glacial acetic acid yields, for example, PHENACETIN (Acetyl-*p*-phenetidine), $CH_3 \cdot CO \cdot NH \cdot C_6H_4 \cdot OC_2H_5$, **Phenetole** being $C_6H_5 \cdot OC_2H_5$. Phenacetin is used as an antipyretic and antineuralgic and forms colourless and tasteless white crystals, m.pt. 135°, which are soluble in alcohol and slightly so in water. It costs about 6*s*. per kilo.

DIAMINOPHENOL (1 : 2 : 4) is obtained from the dinitrophenol and forms the photographic developer, *amidol* (*see above*).

DIHYDROXYDIAMINOARSENOBENZENE is the product prepared by Ehrlich and Bertheim as hydrochloride and placed on the market in 1910 under the name *salvarsan* or *606*. It is a straw-yellow powder, dissolving in water to an acid solution, and it contains 34 per cent. of arsenic. It also bears the name *Hata*, since it was Dr. Hata, of the Ehrlich Institute, who first injected it into animals and found it to be highly efficacious in cases of syphilis in rabbits, who were able to withstand a certain dose of the preparation. It was applied to man by Alt in the case of a syphilitic paralytic, and was subsequently largely used with success by Iversen.

Salvarsan is a specific remedy for syphilis, the spirochetes being killed in 24 to 48 hours and the syphilitic symptoms disappearing rapidly even where treatment with mercury or iodine is without effect. The cure seems, however, to be very painful, relapse and secondary effects sometimes occurring. The firm of Meister, Lucius und Brüning (Höchst, near Frankfort), who make salvarsan, sold a million pounds' worth of it in 1911.

THIOPHENOL (Phenyl Hydrosulphide), $C_6H_5 \cdot SH$, is obtained by heating phenol with phosphorus pentasulphide or by reducing benzenesulphonic chloride, $C_6H_5 \cdot SO_2Cl$. It is a liquid of very unpleasant odour and exhibits the characters of the mercaptans.

It readily forms salts, that of mercury, $(C_6H_5S)_2Hg$, for example, crystallising in needles. When oxidised in ammoniacal solution, thiophenol yields **Phenyl Disulphide**, $(C_6H_5)_2S_2$, melting at 60°.

Phenyl Sulphide, $(C_6H_5)_2S$, is obtained from thiophenol and diazobenzene chloride, and has an alliaceous odour.

AMINOTHIOPHENOLS, $NH_2 \cdot C_6H_4 \cdot SH$. The ortho-compound readily forms condensation products of the type $C_6H_4\left\langle {N \atop S} \right\rangle CH$, or of greater complexity, such as *primuline* (a yellow dye diazotised on the fibre), which is obtained by heating p-toluidine with sulphur and then sulphonating. When heated with sodium sulphide and sulphur, p-aminophenol yields *Vidal black*, which colours cotton in an alkaline and reducing bath of sodium sulphide. The black thus obtained is brilliant and stable, like most of these *sulphur dyes*.

PHENOLSULPHONIC ACID, $OH \cdot C_6H_4 \cdot SO_3H$, is obtained from phenol and concentrated sulphuric acid or, better, from benzenesulphonic acid. The ortho- and para-compounds are preferably formed, and the former is transformed into the latter on heating. The meta-derivative is prepared indirectly. The ortho-compound is used as an antiseptic under the name *sozolic acid* or *aseptol*.

I. AZO-, DIAZO-, AND DIAZOAMINO-COMPOUNDS AND HYDRAZINES

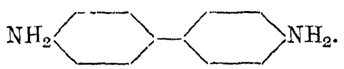
1. AZO-DERIVATIVES

These are intermediate reduction products of nitro-compounds and contain a characteristic group of two nitrogen atoms, each of which is united to an aromatic group.

In acid solution hydrogen reduces nitro-derivatives directly to aromatic amines, but in *alkaline* solution two benzene nuclei condense and become joined by two nitrogen atoms. In this way the following compounds can be obtained from nitrobenzene : (1) **Azoxybenzene**, $C_6H_5 \cdot \underbrace{N — N}_{O} \cdot C_6H_5$; (2) **Azobenzene**, $C_6H_5 \cdot N : N \cdot C_6H_5$; (3) **Hydrazobenzene**, $C_6H_5 \cdot NH \cdot NH \cdot C_6H_5$. Reduction of nitrobenzene with zinc dust in neutral solution yields **Phenylhydroxylamine**, $C_6H_5 \cdot NH \cdot OH$.

When aliphatic amines are oxidised, the alkyl groups are detached in the form of acids and ammonia is generated, but the aromatic amines yield important intermediate compounds, *e.g.* azoxy-derivatives.

AZOBENZENE (Benzeneazobenzene), $C_6H_5 \cdot N : N \cdot C_6H_5$, is obtained by reducing nitrobenzene with a solution of stannous chloride in excess of potassium hydroxide or by distilling azoxybenzene with iron filings. It forms orange-red crystals melting at 68° and boils at 295° without decomposition ; it is insoluble in water and is volatile in steam. On reduction in acid solution it yields benzidine :



Higher homologues, such as **Azotoluene**, are also known.

AZOXYBENZENE is formed by oxidising aniline with potassium permanganate in alkaline solution or, better, by boiling nitrobenzene with alcoholic potash. It forms pale yellow crystals melting at 36°. When heated with concentrated sulphuric acid, it is converted into **HYDROXYAZOBENZENE** :

$$C_6H_5 \cdot \underbrace{N - N}_{O} \cdot C_6H_5 \longrightarrow C_6H_5 \cdot N : N \cdot C_6H_4 \cdot OH.$$

Hydroxyazo-compounds are formed also by the action of diazo-compounds on phenols (especially resorcinol and the naphthols) in presence of alkali :

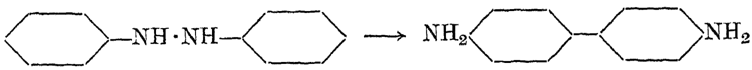
$$C_6H_5 \cdot N_2 \cdot Cl + C_6H_5 \cdot OK = C_6H_5 \cdot N : N \cdot C_6H_4 \cdot OH + KCl.$$

These compounds form yellow, red, or brown crystals, readily soluble in alcohol but insoluble in water. They are azo-dyes (*tropæolins*).

AMINOAZOBENZENES are obtained by the following methods, which introduce the amino-group into the para-position. *Aminoazobenzene* itself is formed by nitrating azobenzene and reducing the mononitroazobenzene thus obtained ; or by transposition of the diazoamino-compounds (*see* p. 569), and hence indirectly from diazobenzene and a primary or secondary amine ; or by *coupling* diazo-compounds with tertiary amines, in which case the aminic hydrogen of the aminoazo-compounds is substituted. If the aminic group cannot enter the para-position, owing to this being occupied, the reaction becomes more difficult and o-aminoazo-derivatives are formed. The interaction of diazo-compounds with m-diamines yields *diaminoazobenzenes*, which are yellow, red, or brown dyes and are termed **Chrysoidines**, $C_6H_5 \cdot N_2 \cdot Cl + C_6H_4(NH_2)_2 = HCl + C_6H_5 \cdot N : N \cdot C_6H_3(NH_2)_2$ (chrysoidine). The amino-group of p-aminoazobenzenes can also be diazotised, giving diazo-compounds, which again react with amines to form a group of substances called *bisazo-compounds* or *tetrazo-compounds*, *e.g.* $C_6H_5 \cdot N : N \cdot C_6H_4 \cdot N : N \cdot C_6H_4 \cdot NH_2$; trisazo-compounds are also known. These substances are used for *Biebrich scarlet*, croceine, &c.

HYDRAZOBENZENE, $C_6H_5\cdot NH\cdot NH\cdot C_6H_5$, is obtained by reducing azobenzene or nitrobenzene with zinc dust and alcoholic potash, and forms colourless crystals melting at 126°. With energetic reducing agents it gives aniline, while oxidising agents ($FeCl_3$ or atmospheric oxygen) convert it into azobenzene.

Under the action of a strong acid it undergoes transformation, even in the cold, into **Benzidine** (*diaminodiphenyl*):

 (*benzidine*)

which forms a sulphate only slightly soluble in cold water. The formation of benzidine in this way shows that it contains the amino-groups in the para-positions, and this is confirmed by the fact that this transformation does not occur with a hydrazobenzene in which the para-hydrogen is replaced by another group.

Electrolytic Reduction of Nitroderivatives. This has been studied more especially by Gattermann, Haber and Elbs, who found that, in the electrolytic conversion of nitrobenzene to aniline in acid solution, various intermediate products are formed, the *primary* ones being:

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} \longrightarrow \underset{\text{Nitrosobenzene}}{C_6H_5\cdot NO} \longrightarrow \underset{\text{Phenylhydroxylamine}}{C_6H_5\cdot NH\cdot OH} \longrightarrow \underset{\text{Aniline}}{C_6H_5\cdot NH_2}:$$

while in *alkaline* alcoholic solution two secondary reactions occur, the nitrosobenzene first formed reacting with the phenylhydroxylamine formed later, giving azoxybenzene:

$$C_6H_5\cdot NH\cdot OH + C_6H_5\cdot NO = H_2O + C_6H_5\cdot \underset{\diagdown O \diagup}{N - N}\cdot C_6H_5,$$

this being subsequently reduced to hydrazobenzene, which reacts with the excess of nitrobenzene, forming azobenzene and azoxybenzene.

The reduction of hydrazobenzene to aniline requires a tension at the cathode much greater than suffices for the formation of nitrosobenzene and phenylhydroxylamine; with 1·47 volts, only traces of aniline are formed.

2. DIAZO-DERIVATIVES

In the diazo-compounds of the aromatic series (discovered by P. Griess in 1860) the characteristic group, $-N_2-$, is united to only one aromatic radical (*aryl, Ar*) and to an acid residue (X). This group therefore forms two series of compounds.

(1) *Diazonium* salts, in which one atom of nitrogen is pentavalent as in ammonium salts. Hantzsch showed their structure to be: $\begin{array}{l}Ar\cdot N : N.\\ \;\;\;\;\;\;| \\ \;\;\;\;\;\;X\end{array}$

(2) True *diazo-compounds* with two trivalent nitrogen atoms, $Ar\cdot N : N\cdot X$; these exist in two stereoisomeric forms (*see* p. 22), the somewhat unstable *syn-diazo*-compounds, $\begin{array}{r}Ar\cdot N\\ \| \\ X\cdot N\end{array}$, and the stable *anti-diazo*-compounds, $\begin{array}{l}Ar\cdot N\\ \;\;\;\;\;\| \\ \;\;\;\;\;N\cdot X\end{array}$. The two groups Ar and X are far apart in the *anti*-compounds, so that they cannot easily react, these compounds hence being the more stable. The cyanide of *antidiazo-p-chlorobenzene*, $\begin{array}{l}Cl\cdot C_6H_4\cdot N\\ \;\;\;\;\;\;\;\;\;\;\;\;\| \\ \;\;\;\;\;\;\;\;\;\;\;\;N\cdot CN\end{array}$, is not decomposed by powdered copper and, on the other hand, cannot have the constitution of a diazonium salt, $\begin{array}{l}Cl\cdot C_6H_4\cdot N : N,\\ \;\;\;\;\;\;\;\;\;\;\;\;| \\ \;\;\;\;\;\;\;\;\;\;\;CN\end{array}$ which, like ammonium salts, should be colourless (whereas

the cyanide is yellow) and should have an alkaline reaction and conduct the electric current in aqueous solution ; neither of these properties is shown by this cyanide, although they are found with the analogous *diazoanisole* cyanide,
$$\begin{array}{l} CH_3O\cdot C_6H_6\cdot N \vdots N. \\ \quad\quad\quad\quad\;\; \dot{C}N \end{array}$$

The *antidiazotates* behave partly like acids and the corresponding *pseudo-acids.* Indeed, antidiazo-hydrate gives the reaction for hydroxyl and forms a conducting aqueous solution ; it is unstable and is converted by acids into the *nitrosamine* (pseudo-acid), which no longer gives the reactions for hydroxyl, does not conduct, has a neutral reaction, and in dry ethereal solution does not form the ammonium salt with ammonia (as, for example, **Phenylnitromethane** does). By alkali the nitrosamine is immediately reconverted into the antidiazotate :

$$\begin{array}{ccc} \begin{array}{c} Ar\cdot N \\ \| \\ N\cdot OH \end{array} & \longrightarrow & \begin{array}{c} Ar\cdot N\cdot H \\ | \\ N:O \end{array} \\ \text{Antidiazotate} & & \text{Nitrosamine} \end{array}$$

Preparation. The gradual addition of sodium nitrite (1 grm.-mol.) solution to a solution of the salt of the amine (1 grm.-mol.) cooled with ice results in the formation of the soluble diazonium salt :

$$\underset{\text{Aniline nitrate}}{C_6H_5\cdot NH_2, HNO_3} + NO\cdot OH = 2H_2O + \underset{\text{Phenyldiazonium nitrate}}{C_6H_5\cdot N_2\cdot NO_3.}$$

$$\underset{\text{Aniline hydrochloride}}{C_6H_5\cdot NH_2, HCl} + NO\cdot OH = 2H_2O + \underset{\text{Phenyldiazonium chloride}}{C_6H_5\cdot N_2\cdot Cl.}$$

These diazonium salts are highly explosive when dry, so that they are always used in aqueous solution, when they are completely harmless.

In these compounds the group $C_6H_5\cdot N_2\cdot$ behaves like the ammonium cation and with strong mineral acids gives neutral salts, while the salts formed with carbonic acid have alkaline reactions, since, like the alkaline carbonates (*see* vol. i, pp. 91 and 436), they readily undergo hydrolytic dissociation.

These salts have extremely high conductivities, and hence are dissociated like potassium and ammonium chlorides, and like these, too, they form *diazonium platinichloride,* $(C_6H_5\cdot N_2\cdot Cl)_2PtCl_4$. The hydroxide, $C_6H_5\cdot N_2\cdot OH$ (from the chloride + AgOH), is known, although it has not yet been isolated ; it is soluble, colourless, and strongly alkaline. All these reactions indicate the existence of a pentavalent nitrogen atom in the group N_2. Two constitutional formulæ are hence possible : $C_6H_5\cdot N \vdots NX$ and $\begin{array}{l} C_6H_5\cdot N \vdots N \\ \quad\quad\quad\; | \\ \quad\quad\quad\; X \end{array}$; various reactions indicate the latter to be the more probable (*see above*).

There are various ways of eliminating the nitrogen from diazo-compounds in the free state, union taking place between the benzene nucleus and the other group joined to the N_2 complex :

(*a*) By heating the aqueous solution of a diazonium salt a phenol is formed : $C_6H_5\cdot N_2\cdot Cl + H_2O = C_6H_5\cdot OH + N_2 + HCl.$

(*b*) When a diazonium salt is heated with alcohol the benzene nucleus unites with the alkoxy-group :

$$C_6H_5\cdot N_2\cdot HSO_4 + C_2H_5\cdot OH = C_6H_5\cdot O\cdot C_2H_5 + N_2 + H_2SO_4 ;$$

under certain conditions, however, the alcohol is oxidised and aldehyde liberated along with the nitrogen :

$$\underset{\text{p-Nitrodiazobenzene chloride}}{NO_2\cdot C_6H_4\cdot N_2\cdot Cl} + C_2H_5\cdot OH = C_6H_5\cdot NO_2 + N_2 + HCl + \underset{\text{Acetaldehyde}}{CH_3\cdot CHO.}$$

(c) When a diazonium chloride is treated with cuprous chloride dissolved in concentrated hydrochloric acid (Sandmeyer), the chlorine (or other halogen) is introduced into the nucleus : $C_6H_5\cdot N_2Cl = C_6H_5\cdot Cl + N_2$. The same result is produced by finely divided copper, which, however, acts catalytically (Gattermann).

(d) The cyanogen group is introduced into the nucleus by the action of potassium salt in presence of a copper compound :

$$C_6H_5\cdot N_2Cl + KCN = KCl + N_2 + \underset{\text{Benzonitrile}}{C_6H_5\cdot CN}.$$

This is a general reaction for obtaining (by subsequent hydrolysis) *aromatic acids*.

(e) Dry diazobenzene chloride, when treated with benzene in presence of aluminium chloride, gives *diphenyl :*

$$C_6H_5N_2Cl + C_6H_6 = N_2 + HCl + C_6H_5\cdot C_6H_5.$$

With tertiary amines, diazonium salts condense in the para-position, giving *aminoazo-derivatives :*

$$C_6H_5N_2Cl + C_6H_5N(CH_3)_2 = HCl + C_6H_5\cdot N : N\cdot C_6H_4(CH_3)_2.$$

Diazonium salts also form hydroxyazobenzenes (*see* p. 565).

DIAZOBENZENE CHLORIDE (Phenyldiazonium Chloride), $C_6H_5\cdot N_2\cdot Cl$, forms colourless needles soluble in water and is obtained by the action of moist AgCl on the corresponding bromide ; the *bromide* is obtained in nacreous scales by the interaction of ethereal solutions of bromine and diazoaminobenzene (tribromoaniline remains in the solution).

DIAZOBENZENE NITRATE (Phenyldiazonium Nitrate), $C_6H_5\cdot N_2\cdot NO_3$, is the salt which is most widely used, and is obtained by passing nitroso-nitric fumes into a cold ethereal solution of diazoaminobenzene or into an aqueous paste of aniline nitrate until this is dissolved ; to the filtered liquid are added the triple volume of alcohol and then ether until the nitrate separates in colourless needles. It is readily soluble in water but insoluble in ether, benzene, chloroform, &c. It has a strong acid reaction and is easily exploded by shock.

DIAZOBENZENE SULPHATE (Phenyldiazonium Sulphate), $C_6H_5\cdot N_2\cdot HSO_4$, is best obtained by treating a concentrated solution of crude diazobenzene nitrate with moderately concentrated sulphuric acid, precipitating several times with excess of alcohol and with ether, and allowing to crystallise in a desiccator. It forms crystals which are readily soluble in water and deflagrate at 100°.

DIAZOBENZENE PERBROMIDE, $C_6H_5\cdot N_2\cdot Br_3$, is prepared by the action of hydrobromic acid and bromine water on diazobenzene salts.

DIAZOBENZENESULPHONIC ACID, $C_6H_4\left\langle\begin{matrix}N_2\cdot OH\\ SO_3H\end{matrix}\right.$, is known as anhydride, $C_6H_4\left\langle\begin{matrix}N_2\\ |\\ SO_3\end{matrix}\right.$, and is obtained by adding a mixture of sodium sulphanilate and sodium nitrite to dilute sulphuric acid. It forms white needles readily soluble in water, and is used to prepare azo-dyes.

With KOH, *phenyldiazonium hydroxide* forms a potassium compound, $C_6H_5\cdot N_2\cdot OK$, and hence behaves as an acid besides as a base. But as it cannot be assumed that these two functions are exhibited to such marked extents by one and the same substance, Hantzsch supposes that, in aqueous solution, it forms a mixture of *phenyldiazonium hydroxide*, $C_6H_5\cdot\underset{\underset{N}{|||}}{N}\cdot OH$, and *syn-diazobenzene hydroxide*, $C_6H_5\cdot N : N\cdot OH$, so that the general reactions mentioned above would be explained thus :

$$C_6H_5\cdot\underset{\underset{Cl}{|}}{N}\vdots N + H\cdot OH = HCl + C_6H_5\cdot N : N\cdot OH \longrightarrow C_6H_5\cdot OH + N \vdots N.$$

None of the reactions referred to above can be explained well without assuming the passage of *diazonium* salts with pentavalent nitrogen into true diazo-compounds with trivalent nitrogen ($-N=N-$) (*see above*).

3. DIAZOAMINO-DERIVATIVES

These contain the aminodiazo-group, $-N=N-NH-$, and are yellow, crystalline substances which do not combine with acids. They are obtained by adding to diazo-salts (freshly formed in solution) primary or secondary amines, *e.g.* aniline hydrochloride ; the separation of the yellow crystalline mass is hastened by addition of concentrated sodium acetate solution :

$$C_6H_5 \cdot N_2 \cdot Cl + C_6H_5 \cdot NH_2 = HCl + C_6H_5 \cdot N_2 \cdot NHC_6H_5.$$

To 2 mols. of aniline and 3 mols. of hydrochloric acid, kept cool with ice, is slowly added 1 mol. of sodium nitrite, the liquid being then precipitated with concentrated sodium acetate solution.

They are also formed directly from free aniline and nitrous acid, in which case diazobenzene hydroxide must be regarded as an intermediate product :

$$(a)\ C_6H_5 \cdot NH_2 + HNO_2 = H_2O + C_6H_5 \cdot N_2 \cdot OH\ ;$$
$$(b)\ C_6H_5 \cdot N_2 \cdot OH + C_6H_5 \cdot NH_2 = H_2O + C_6H_5 \cdot N_2 \cdot NHC_6H_5.$$

With nitrous acid in acid solution, diazoamino-compounds are converted into diazonium salts, the remaining aminic residue, $-NHC_6H_5$. being diazotised :

$$C_6H_5 \cdot N : N \cdot NHC_6H_5 + HNO_2 + 2HCl = 2H_2O + 2C_6H_5 \cdot N_2Cl.$$

When heated with aniline hydrochloride, diazoaminobenzene solution yields aminoazobenzene, which is a colouring-matter from which others are derived. In this transformation, which is common to all diazoamino-compounds, the aniline hydrochloride acts catalytically and takes no part in the reaction ; the amino-group is carried to the para-position with respect to the diazo-group, or, if this is occupied, to the ortho-position :

$$\underset{\text{Diazoaminobenzene}}{C_6H_5 \cdot N : N \cdot NHC_6H_5} \longrightarrow \underset{\text{Aminoazobenzene}}{C_6H_5 \cdot N : N \cdot C_6H_4 \cdot NH_2}.$$

It has been shown by H. Goldschmidt that the velocity constant of this transformation increases with the amount of the catalyst (aniline hydrochloride), and the catalytic powers of the different amine salts are proportional to their degrees of dissociation in water.

4. HYDRAZINES

These compounds are obtained by reducing diazonium salts with a hydrochloric acid solution of stannous chloride :

$$C_6H_5N_2Cl + 4H = \underset{\text{Phenylhydrazine hydrochloride}}{C_6H_5 \cdot NH \cdot NH_2,\ HCl}.$$

The use of sodium sulphite in place of stannous chloride gives first the diazosulphonate, which, when treated with zinc dust and acetic acid and subsequently boiled with hydrochloric acid, gives phenylhydrazine hydrochloride ; this salt separates out, being only slightly soluble in water and less so in acid.

The three stages of the reaction are as follow :

$$(a)\ \underset{\text{Diazobenzene chloride}}{C_6H_5N_2Cl} + Na_2SO_3 = \underset{\text{Sodium diazobenzenesulphonate}}{C_6H_5 \cdot N_2 \cdot SO_3Na} + NaCl.$$
$$(b)\ C_6H_5 \cdot N_2 \cdot SO_3Na + 2H = \underset{\text{Sodium phenylhydrazinesulphonate}}{C_6H_5 \cdot NH \cdot NH \cdot SO_3Na}.$$
$$(c)\ C_6H_5 \cdot NH \cdot NH \cdot SO_3Na + H_2O = NaHSO_4 + \underset{\text{Phenylhydrazine}}{C_6H_5 \cdot NH \cdot NH_2}.$$

PHENYLHYDRAZINE, $C_6H_5 \cdot NH \cdot NH_2$, is the most important member of this group and has a basic character, forming well-crystallised salts. It is a colourless, oily liquid which turns brown in the air; it dissolves only slightly in water, melts at 17·5°, and boils at 241° with slight decomposition. With energetic reducing agents it forms aniline and ammonia, and with oxidising agents (*e.g.* chloride of lime) it can form diazonium compounds, but usually nitrogen is eliminated with formation of water and benzene. It gives characteristic reactions with *lactones*, *sugars*, *aldehydes*, and *ketones* (*see* pp. 206 and 210).

The constitution of phenylhydrazine is proved by the fact that nitrosomethylaniline, $C_6H_5 \cdot N(CH_3) \cdot NO$ (obtained from the secondary amine, methylaniline, $C_6H_5 \cdot NH \cdot CH_3$, by the action of nitrous acid), on reduction, yields *as.phenylmethylhydrazine*, $C_6H_5 \cdot N(CH_3) \cdot NH_2$, which can also be obtained from phenylhydrazine by the action of metallic sodium (this replaces the iminic hydrogen) and subsequently of methyl iodide:

$$C_6H_5 \cdot NH \cdot NH_2 \longrightarrow \underset{\displaystyle \text{Na}}{C_6H_5 \cdot \overset{}{N} \cdot NH_2} \longrightarrow \underset{\displaystyle CH_3}{C_6H_5 \cdot N \cdot NH_2}.$$

Replacement of the aminic hydrogen by an acid residue yields *hydrazides* (α and β), which give a reddish violet coloration with sulphuric acid and potassium dichromate. The hydrazides are insoluble in water and may hence be used for the precipitation of soluble acids.

DIPHENYLHYDRAZINE, $(C_6H_5)_2N \cdot NH_2$, is obtained by reducing **Diphenylnitrosamine**, $(C_6H_5)_2N \cdot NO$, in alkaline solution with zinc dust and acetic acid. It is a base boiling at 34° almost without decomposition, and oxidising readily in the air; its salts are unstable. It is insoluble in water and hence reduces Fehling's solution only slightly, even in the hot. With concentrated sulphuric acid it gives a blue coloration. The action of oxidising agents distinguishes it from the isomeric hydrazobenzene; the latter gives azobenzene, whilst diphenylhydrazine yields in the cold **Tetraphenyltetrazone**, $(C_6H_5)_2N \cdot N : N \cdot N(C_6H_5)_2$, and in the hot diphenylamine and violet colouring-matters with abundant evolution of nitrogen. With nitrous acid, hydrazobenzene forms nitroso-derivatives, whilst diphenylhydrazine, like other secondary hydrazines, gives diphenylnitrosamine and nitrous oxide.

BENZYLPHENYLHYDRAZINE, $C_6H_5 \cdot CH_2 \cdot N(C_6H_5) \cdot NH_2$, is obtained from phenylhydrazine and benzyl chloride. **Benzylhydrazine**, $C_6H_5 \cdot CH_2 \cdot NH \cdot NH_2$, boiling at 135° (*in vacuo*), is also known.

p-**NITROPHENYLHYDRAZINE**, obtained from *p*-nitraniline, forms yellow crystals and is a useful reagent for aldehydes and ketones.

β-**PHENYLHYDROXYLAMINE**, $C_6H_5 \cdot NH \cdot OH$, is obtained by the gentle oxidation of aniline or the cautious reduction of nitrobenzene with zinc dust and water, and forms colourless crystals melting at 81°. With oxygen it gives *p*-aminophenol, with oxygen azoxybenzene and with dichromate nitrosobenzene. The α-isomeride, $NH_2 \cdot OC_6H_5$, is of little importance.

L. AROMATIC ALCOHOLS, ALDEHYDES, AND KETONES

In these compounds the primary alcohol group, the aldehyde group, or the ketonic group forms a side-chain to the benzene nucleus and shows all the general properties of these groups. Di- and trihydric alcohols are also known, *e.g.* **Phthalic Alcohol** (ortho); **Xylylene Alcohol** (para), $C_6H_4(CH_2 \cdot OH)_2$; **Phenylglycerol**, $C_6H_5 \cdot CH(OH) \cdot CH(OH) \cdot CH_2 \cdot OH$.

BENZYL ALCOHOL, $C_6H_5 \cdot CH_2 \cdot OH$ (discovered by Cannizzaro in 1853), is isomeric with the cresols, $CH_3 \cdot C_6H_4 \cdot OH$, and is obtained by the interaction of benzyl chloride and potassium acetate and subsequent hydrolysis of the acetyl-derivative thus obtained, or, better, by the action of aqueous potassium hydroxide on benzaldehyde:

$$2C_6H_5 \cdot CHO + KOH = C_6H_5 \cdot CO_2K + C_6H_5 \cdot CH_2 \cdot OH.$$

The alcohol readily gives benzyl chloride when treated with PCl_5. On oxidation

it gives first benzaldehyde and then benzoic acid, its constitution being thus proved. It forms simple and mixed ethers and esters. It differs from aliphatic alcohols by resinifying with sulphuric acid. It has the characters of a true alcohol and is hence insoluble in alkali (unlike the phenols). It is slightly soluble in alcohol and boils at 206°.

Various higher *homologues* are known: **Tolylene Alcohols**, $CH_3 \cdot C_6H_4 \cdot CH_2 \cdot OH$; **Cumyl Alcohol** (p-), $C_3H_7 \cdot C_6H_4 \cdot CH_2 \cdot OH$, &c.

Styryl Alcohol, $C_6H_5 \cdot CH : CH \cdot CH_2 \cdot OH$, containing an unsaturated side-chain, is found as ester (styracin) in storax; it forms acicular crystals with an odour of hyacinth.

With alcoholic potash *aromatic aldehydes* are partly oxidised and partly reduced, benzaldehyde, for instance, being converted into potassium benzoate and benzyl alcohol:

$$2C_6H_5 \cdot CHO + KOH = C_6H_5 \cdot CO_2K + C_6H_5 \cdot CH_2 \cdot OH.$$

With dimethylaniline or phenol these aldehydes give derivatives of **Triphenylmethane**:

$$C_6H_5 \cdot CHO + 2C_6H_5 \cdot OH = H_2O + C_6H_5 \cdot CH\begin{cases} C_6H_4 \cdot OH \\ C_6H_4 \cdot OH. \end{cases}$$

BENZALDEHYDE, $C_6H_5 \cdot C\begin{cases} {}^{/\!/}O \\ \diagdown H \end{cases}$, occurs in the **Amygdalin**, $C_{20}H_{27}NO_{11}$, of bitter almonds in the form of a glucoside. It is a liquid of pleasant odour and dissolves slightly in water; it boils at 179°, has the sp. gr. 1 05 and forms *bitter almond oil*. It oxidises easily and forms crystalline products with bisulphites, while it combines with hydrogen, hydrogen cyanide, &c., forming an oxime, a hydrazone, &c. With ammonia it gives **Hydrobenzamide**, $3C_6H_5 \cdot CHO + 2NH_3 = 3H_2O + (C_6H_5 \cdot CH)_3N_2$. It is formed by distilling a mixture of calcium formate and benzoate and also by oxidising benzyl alcohol.

Until recently it was prepared industrially by heating benzal chloride under pressure with milk of lime and calcium carbonate:

$$C_6H_5 \cdot CHCl_2 + Ca(OH)_2 = CaCl_2 + C_6H_5 \cdot CHO + H_2O.$$

Nowadays, however, it is obtained more conveniently by treating benzene with a gaseous mixture of carbon monoxide and hydrogen chloride in presence of Cu_2Cl_2 or $AlBr_3$ (Ger. Pat. 126,241).

Pure benzaldehyde may also be readily obtained by oxidising toluene (*e.g.* with PbO_2 and H_2SO_4), a mixture of 40 per cent. of the aldehyde with 60 per cent. of unaltered toluene being obtained (Ger. Pat. 154,499). One hundred kilos of this mixture and 400 litres of water are treated with sulphur dioxide until about 26 per cent. is absorbed. In this way all the aldehyde passes into solution (improvement on the use of sodium bisulphite) and can be decanted from the undissolved toluene. It is then sufficient to heat the sulphurous solution slowly from 30° to 100° to eliminate all the sulphur dioxide which is passed into a further portion of the aldehyde mixture. After cooling the solution, almost the whole of the benzaldehyde is obtained in a pure state and the mother-liquors are utilised in succeeding operations so that the small amounts of aldehyde remaining dissolved may not be lost.

Commercial benzaldehyde and that for industrial uses costs about 3*s.*, the pure product about 4*s.*, and the chemically pure about 9*s.* 6*d.* per kilo. For industrial purposes, it should have a specific gravity of 1·052 to 1·054, and should distil completely in a current of hydrogen between 176° and 180°. Its solution in concentrated sulphuric acid should be only slightly brown and it should dissolve completely in sodium bisulphite. Any benzoic acid present can be titrated with phenolphthalein as indicator.

HOMOLOGUES OF BENZALDEHYDE are obtained by treating aromatic hydrocarbons with gaseous hydrogen chloride and carbon monoxide in presence of $AlCl_3$ or Cu_2Cl_2. The first product obtained under these conditions is probably formyl chloride, which then reacts thus:

$$X \cdot C_6H_5 + Cl \cdot CHO = HCl + X \cdot C_6H_4 \cdot CHO.$$

Aldehydes are also obtained from ethyl chloroxalate and aromatic hydro-

carbons in presence of $AlCl_3$, the ketonic ester obtained being hydrolysed and the acid subjected to dry distillation in order to expel CO_2:

$$X\cdot C_6H_5 + Cl\cdot CO\cdot COOC_2H_5 = HCl + X\cdot C_6H_4\cdot CO\cdot COOC_2H_5;$$
$$X\cdot C_6H_4\cdot CO\cdot COOC_2H_5 = X\cdot C_6H_4\cdot CHO + CO_2.$$

The action of HCl and HCN on aromatic hydrocarbons also yields aldehydes, *aldines* being formed as intermediate products:

$$C_6H_6 + HCN + HCl = \underset{\text{Benzaldine Hydrochloride}}{C_6H_5\cdot CH:NH, HCl}.$$
$$C_6H_5\cdot CH:NH, HCl + H_2O = C_6H_5\cdot CHO + NH_4Cl.$$

CINNAMALDEHYDE, $C_6H_5\cdot CH:CH\cdot CHO$, is an oil of pleasant odour, boiling at 246°; it is volatile in steam and is separated from cinnamon oil, of which it is the chief constituent, by means of sodium bisulphite.

NITROBENZALDEHYDES, $NO_2\cdot C_6H_4\cdot CHO$, are prepared in various ways. The ortho-compound is obtained either from *o*-nitrobenzyl chloride or by oxidising *o*-nitrotoluene. It forms colourless crystals melting at 46° and with acetone and caustic soda leads to the synthesis of indigo.

Nitration of benzaldehyde yields mainly the m-compound, together with 20 per cent. of the o-derivative.

CUMINALDEHYDE (Cuminol, Isopropylbenzaldehyde), $C_3H_7\cdot C_6H_4\cdot CHO$, occurs in Roman cumin oil.

AROMATIC KETONES

ACETOPHENONE, $C_6H_5\cdot CO\cdot CH_3$, is obtained by distilling calcium acetate with calcium benzoate or, better, by treating benzene with acetyl chloride in presence of $AlCl_3$.

It forms crystals melting at 20° and boils at 200°; it dissolves only slightly in water, has a pleasant smell, and is used as a hypnotic under the name of **hypnone**. On oxidation it gives either benzylformic acid or benzoic acid and carbon dioxide; halogens give products substituted in the side-chain.

BENZOPHENONE (Diphenyl Ketone), $C_6H_5\cdot CO\cdot C_6H_5$, is obtained either by the dry distillation of calcium benzoate or by the action of benzoyl chloride on benzene in presence of $AlCl_3$. Its behaviour is similar to that of aliphatic compounds, and with hydrogen it forms **Benzhydrol**, $C_6H_5\cdot CH(OH)\cdot C_6H_5$, and **Benzopinacone**, $(C_6H_5)_2 = \underset{\displaystyle OH}{\underset{|}{C}} - \underset{\displaystyle OH}{\underset{|}{C}} = (C_6H_5)_2$.

When fused with potassium hydroxide, it gives benzene and potassium benzoate:

$$C_6H_5\cdot CO\cdot C_6H_5 + KOH = C_6H_6 + C_6H_5\cdot COOK.$$

Benzophenone exists in two modifications which differ physically: an unstable form, m.pt. 27°, and a stable form, m.pt. 49°.

DIPHENYLENEKETONE, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!CO$, is the ketone corresponding with diphenylene-methane (*see later*), and is obtained by heating phenanthraquinone with lime. With nascent hydrogen it gives **Fluorene Alcohol**, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!CH\cdot OH$ (colourless scales, m.pt. 153°), and, when fused with potash, **Diphenylcarboxylic Acid**, $C_6H_5\cdot C_6H_4\cdot CO_2H$.

Polyacetones, such as **Benzoylacetone**, $C_6H_5\cdot CO\cdot CH_2\cdot CO\cdot CH_3$, and **Acetophenone-acetone**, $C_6H_5\cdot CO\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3$, are also known.

Condensation of benzaldehyde with acetophenone or acetone in presence of NaOH gives unsaturated ketones: **Benzalacetone**, $C_6H_5\cdot CH:CH\cdot CO\cdot CH_3$ (m.pt. 41°); **Benzalacetophenone** (*chalkone*), $C_6H_5\cdot CH:CH\cdot CO\cdot C_6H_5$ (m.pt. 58°).

AROMATIC OXIMES present interesting cases of isomerism (*see* pp. 22 and 210). Thus, **Benzaldoxime** is known in two forms: liquid *anti-benzaldoxime*, which boils unaltered, and solid *syn-benzaldoxime*, which readily loses water

(with acetic anhydride), forming benzonitrile :
$$\begin{array}{l}C_6H_5\cdot C\cdot H = H_2O + C_6H_5\cdot C \vdots N.\\ \qquad\quad \|\\ \qquad\quad N\cdot OH\end{array}$$
Under these conditions the anti-aldoxime gives an acetyl-derivative, so that the two aldoximes can be distinguished in this way.

With *ketoximes* two isomerides are formed *only* when the two groups united to the carbonyl group are different :

$$\begin{array}{c}X - C - X'\\ \|\\ N - OH\\ \textit{syn}\end{array} \qquad \text{and} \qquad \begin{array}{c}X - C - X'\\ \|\\ OH - N\\ \textit{anti}\end{array}$$

Thus, Benzophenonoxime, $\begin{array}{c}C_6H_5 - C - C_6H_5\\ \|\\ N - OH\end{array}$, does not form isomerides, which are, however, obtained if a hydrogen atom of one of the benzene groups is replaced by a halogen, alkyl group, &c.

The *ketoximes* show Beckmann's transposition,[1] in which the isomeric ketoximes, which have different melting-points, give rise to two different substituted amides according as the transposition takes place with the group X or X′ (*see Note*).

BENZALAZINE, $C_6H_5\cdot CH : N\cdot N : CH\cdot C_6H_5$, is obtained by the condensation of 2 mols. of benzaldehyde with 1 mol. of hydrazine (sulphate), and forms yellow crystals melting at 93°.

BENZALDEHYDEPHENYLHYDRAZONE, $C_6H_5\cdot CH : N\cdot NHC_6H_5$, forms colourless crystals melting at 132° and forms stereoisomerides.

M. AROMATIC HYDROXY-ALCOHOLS, HYDROXY-ALDEHYDES, AND KETONIC ALCOHOLS

$C_6H_4<{OH \atop CH_2\cdot OH}$ $\left\{\begin{array}{l}\text{o} = \textit{saligenin}\\ \text{m}\\ \text{p}\end{array}\right.$ $\left.\begin{array}{l}\\ \\ \end{array}\right\}$ *hydroxybenzyl alcohols*

$C_6H_4<{OH \atop CHO}$ $\left\{\begin{array}{l}\text{o} = \textit{salicylaldehyde}\\ \text{m}\\ \text{p}\end{array}\right.$ $\left.\begin{array}{l}\\ \\ \end{array}\right\}$ *hydroxybenzaldehydes*

$C_6H_3\begin{array}{l}\diagup OH \quad 4\\ - OH \quad 3\\ \diagdown CHO \quad 1\end{array}$ *protocatechuic aldehyde*

$C_6H_4<{OCH_3 \atop CH_2\cdot OH}$ p = *anisic alcohol* (m.pt. 45°, b.pt. 259°)

$C_6H_4<{OCH_3 \atop CHO}$ p = *anisaldehyde*

$C_6H_3\begin{array}{l}\diagup OH \quad 4\\ - OCH_3 \quad 3\\ \diagdown CH_2\cdot OH \quad 1\end{array}$ *vanillic alcohol*

$C_6H_3\begin{array}{l}\diagup OH \quad 4\\ - OCH_3 \quad 3\\ \diagdown CHO \quad 1\end{array}$ *vanillin*

[1] The Beckmann transposition is that obtained with ketoximes in general by treating them with acetyl chloride or concentrated sulphuric acid or, in some cases, merely by fusion. The oxygen of the oxime changes places with a radical united to the ketonic carbon giving a substituted amide, an unstable, tautomeric, hydroxyl compound being probably formed as an intermediate product :

$$\begin{array}{c}X\cdot C\cdot X'\\ \|\\ N\cdot OH\end{array} \longrightarrow \left[\begin{array}{c}X\cdot C\cdot OH\\ \|\\ N\cdot X'\end{array}\right] \longrightarrow \begin{array}{l}X\cdot C.O\\ \;|\\ N<{H \atop X'}\end{array}.$$

The structure of the isomeric syn- and anti-oximes can be determined by Beckmann's reaction. Thus, the above oxime is the anti-compound, the transposition with the syn-isomeride would be as follows

$$\begin{array}{c}X\cdot C\cdot X'\\ \|\\ OH\cdot N\end{array} \longrightarrow \begin{array}{r}O\;\; C\cdot X'\\ |\\ {H \atop X}>N\end{array}$$

The three isomeric hydroxybenzyl alcohols are known, their melting-points being as follow : o-, 82° ; m-, 67° ; p-, 110°. The most common of these is :

SALIGENIN (*o*-Hydroxybenzyl Alcohol, *see above*), $OH \cdot C_6H_4 \cdot CH_2 \cdot OH$, occurring in the glucoside *salicin*, from which it can be obtained by the action of emulsin, ptyalin or dilute acid (Piria, 1845) :

$$C_6H_{11}O_5 \cdot O \cdot C_6H_4 \cdot CH_2 \cdot OH + H_2O = OH \cdot C_6H_4 \cdot CH_2 \cdot OH + C_6H_{12}O_6 \text{ (glucose)}.$$

It is soluble in alcohol, ether, or boiling water and gives a dark blue coloration with ferric chloride.

AROMATIC HYDROXYALDEHYDES, or phenolic aldehydes, are obtained (1) by the action of chloroform and caustic potash on phenols: $C_6H_5 \cdot OH + 4KOH + CHCl_3 = 3KCl + 3H_2O + CHO \cdot C_6H_4 \cdot OK$; or (2) by the action of hydrocyanic and hydrochloric acids on phenols in presence of aluminium chloride or zinc chloride, *aldim* hydrochlorides being formed as intermediate products.

With difficulty by oxidising agents, but readily by fusion with alkali, these aldehydes give the corresponding hydroxycarboxylic acids. They reduce ammoniacal silver solution but *not Fehling's solution.* With alkali they give soluble alkali phenoxides which form the alkyl derivatives of the phenols when treated with alkyl iodides.

SALICYLALDEHYDE (*o*-Hydroxybenzaldehyde), $OH \cdot C_6H_4 \cdot CHO$, is found in the volatile oil of *Spiræa ulmaria.* Its synthesis by means of chloroform is indicated above and it is separated from the p-aldehyde formed at the same time by distillation in steam. It is a liquid, b.p. 196°, sp. gr. 1·172 at 15° ; it dissolves to some extent in water and gives a violet coloration with ferric chloride. Like all o-hydroxy-aldehydes it colours the skin yellow.

ANISALDEHYDE (*see above*) is obtained by the cautious oxidation of Anethole, $CH_3 \cdot CH : CH \cdot C_6H_4 \cdot OCH_3$, with dichromate and sulphuric acid, the aldehyde being distilled in steam and purified by means of sodium bisulphite. It boils at 248°, has sp. gr. 1·123 at 15°, and, owing to its strong odour of hawthorn, is used in perfumery (price 20*s.* per kilo).

VANILLIN, $C_6H_3(OH)(OCH_3)(CHO)$ 4 : 3 : 1 (*m*-Methoxy-*p*-hydroxybenzaldehyde), is found (about 2 per cent.) in the pods or fruit of vanilla (*Vanilla planifolia*)[1] and as a glucoside (coniferin, $C_{16}H_{22}O_8 + 2H_2O$) in the sap of the conifers, in asparagus, and in beet-juice ; it is also formed by oxidising the resin of olives.

It is readily obtained artificially by treating clove oil with dilute alkali, which dissolves the eugenol and transforms it into Isoeugenol, $C_6H_3(OH)(OCH_3)(CH : CH \cdot CH_3)$, which is then oxidised by ozone or permanganate. It forms slender white crystals which melt at 80-81° and sublime, and it boils at 285°. It has a strong odour of vanilla and now costs about 36*s.* per kilo, although twenty years ago its price was several hundreds of pounds per kilo.

By HCl at 200° it is transformed into protocatechuic aldehyde, the methylene ether of which constitutes Piperonal (*heliotropin* or artificial heliotrope),

$$\begin{array}{l} CH : CH \cdot C \cdot O \diagdown \\ \;| \qquad\quad \| \qquad\; CH_2, \\ CHO \cdot C : CH \cdot C \cdot O \diagup \end{array}$$

(m.pt. 37° ; b.pt. 263°), costing from 16*s.* to 28*s.* per kilo, according to its purity.

BENZOYLCARBINOL, $C_6H_5 \cdot CO \cdot CH_2 \cdot OH$, obtained from Phenacyl Bromide, $C_6H_5 \cdot CO \cdot CH_2Br$, forms stable, shining scales, and possesses strong reducing properties. The corresponding acetonaldehyde is Phenylglyoxal, $C_6H_5 \cdot CO \cdot CHO$, analogous to pyruvic aldehyde.

[1] Vanilla is a climbing, herbaceous plant growing well in Mexico and in Réunion. The fruit is fleshy and cylindrical (10 to 30 cm. long) and contains a number of round black seeds with a pleasant odour. The fruit is gathered before it is quite ripe, as otherwise the pods open and the seeds are lost. Their vitality is destroyed by steeping them in water at 80° to 85° or placing them in an oven at 50° to 70° or in the sunlight. The capsules thus turn dark brown and after being allowed to sweat for 20 to 30 days at 30° to 40° they become covered with a crystalline, perfumed powder. They are then tied up in bundles of 50 and sold in boxes holding 3 to 10 kilos at 20*s.* to 64*s.* per kilo. Of inferior quality are the smaller fruit and those from the Antilles, Brazil, and Guiana. They are used for pastry, liquors, perfumes, and chocolates. The United States imported 400 tons (£247,200) of vanilla pods in 1910 and 500 tons (£427,400) in 1911.

N. AROMATIC ACIDS

Like the aliphatic acids, these form salts, anhydrides, esters, amides, &c., and give in addition other products by substitution in the benzene nucleus.

Here, too, the characteristic group is the carboxyl, COOH, and the acids may be either mono- or poly-basic, according to the number of carboxyl groups, this being indicated in the name :

$C_6H_5\cdot COOH$	$C_6H_4(COOH)_2$	$C_6H_3(COOH)_3$	$C_6(COOH)_6$
Benzoic acid (benzenecarboxylic or benzenemethanoic acid)	Phthalic acids (benzenedicarboxylic or benzenedimethanoic acids)	Benzenetricarboxylic acids (benzenetrimethanoic acids)	Mellitic acid (benzenehexacarboxylic or benzenehexamethanoic acid)

Aromatic acids with unsaturated side-chains are also known, these behaving like unsaturated aliphatic compounds :

$C_6H_5\cdot CH : CH\cdot CO_2H$	$C_6H_5\cdot C \vdots C\cdot CO_2H$
Cinnamic acid	Phenylpropiolic acid

There are also various acids derived from the hydrobenzenes, with characters resembling those of aliphatic compounds.

Aromatic hydroxy-acids with a hydroxyl group in the nucleus behave partly like phenols and partly like acids, and are analogous to the aromatic alcohol-acids containing acid groups and true alcoholic groups in the side-chains.

In each of the aliphatic acids a hydrogen atom can be replaced by a benzene residue, giving aromatic acids of the acetic acid series (*e.g.* **Phenylacetic Acid,** $C_6H_5\cdot CH_2\cdot CO_2H$) and of the glycollic and succinic series, &c.

In general, aromatic acids are crystalline and only slightly soluble in water, while they are often soluble in alcohol or ether. The more simple ones sublime or distil unchanged and lose CO_2 only on distillation with soda-lime, this occurring with the more complex acids simply on heating. Their alkaline salts are soluble in water, but the acids are precipitated in the free state on addition of a mineral acid.

GENERAL METHODS OF FORMATION. (*a*) When hydrocarbons homologous with benzene are oxidised, each side-chain, no matter what its length or nature, yields only a single carboxyl group attached directly to the benzene nucleus. When several lateral chains are present, dilute nitric acid oxidises them gradually, whilst with chromic acid they are all oxidised together: $C_6H_5\cdot CH_3$ gives $C_6H_5\cdot CO_2H$; $C_6H_5\cdot C_2H_5$ gives $C_6H_5\cdot CO_2H$; $C_6H_5\cdot CH : CH\cdot CO_2H$ gives $C_6H_5\cdot CO_2H$; $C_6H_4(CH_3)_2$ gives $C_6H_4(CO_2H)_2$. Of the disubstituted derivatives, the *ortho*-compounds are oxidised very easily and do not give carboxyls unless the oxidation is carried out with great care, *e.g.* with dilute nitric acid or permanganate ; *para*-derivatives are readily oxidised by chromic acid and the *meta*- less readily. Compounds containing a negative group, even OH, in the *ortho*-position are not oxidised even by chromic acid.

(*b*) By oxidising primary alcohols and aldehydes in the usual way.

(*c*) By hydrolysing nitriles : $C_6H_5\cdot CN + 2H_2O = NH_3 + C_6H_5\cdot COOH$. The *nitriles* are formed by distilling, *e.g.* potassium phenylsulphonate with potassium cyanide or ferrocyanide : $C_6H_5\cdot SO_3K + KCN = K_2SO_3 + C_6H_5\cdot CN$ (benzonitrile) or from the chlorides of compounds with side-chains : $C_6H_5\cdot CH_2Cl + KCN = KCl + C_6H_5\cdot CH_2\cdot CN$ (benzyl cyanide). Nitriles can also be obtained from primary amines by diazotising and subjecting the diazo-compounds to Sandmeyer's reaction (*see* p. 568) ; also from the aldehydes by way of the oximes (*see* pp. 199 and 206).

(*d*) By the action of CO_2 on monobromobenzene in presence of sodium

(Kekulé), or by treating benzene or its homologues with phosgene ($COCl_2$) in presence of $AlCl_3$ (Friedel and Krafft):

$$C_6H_5Br + CO_2 + 2Na = C_6H_5 \cdot COONa + NaBr;$$
$$C_6H_6 + COCl_2 = HCl + C_6H_5 \cdot CO \cdot Cl \text{ (which, with } H_2O\text{, gives the acid).}$$

(*e*) **Phenolic Acids** are obtained by the action of CO_2 or CCl_4 and alkali on *sodium phenoxides*:

$$C_6H_5 \cdot ONa + CO_2 = C_6H_4 <^{OH}_{COONa}$$

$$C_6H_5 \cdot ONa + CCl_4 = C_6H_4 <^{OH}_{CCl_3} + NaCl, \text{ and}$$

$$C_6H_4 <^{OH}_{CCl_3} + 4NaOH = 3NaCl + 2H_2O + C_6H_4 <^{OH}_{COONa} \text{ (para).}$$

If chloroform is used in place of carbon tetrachloride, ortho- and para-hydroxyaldehydes are obtained.

(*f*) The syntheses with ethyl acetoacetate or ethyl malonate are analogous to those of the fatty series (*see* pp. 309 and 332) and are carried out with phenols, derivatives with halogens in the side-chain, &c.; complex ketonic acids are obtained which undergo both the acid and the ketonic decomposition.

Aromatic acids with unsaturated side-chains are obtained by the methods used for aliphatic unsaturated acids, or by Perkin's reaction (*see* p. 291) between fatty acids and aromatic aldehydes in presence of acetic anhydride, which removes the water formed:

$$C_6H_5 \cdot CHO + \underset{\text{Sodium acetate}}{CH_3 \cdot CO_2Na} = C_6H_5 \cdot CH : CH \cdot COONa + H_2O.$$

With substituted benzaldehydes a varied series of unsaturated aromatic acids can be obtained.

Also benzal chloride and sodium acetate give unsaturated acids:

$$C_6H_5 \cdot CHCl_2 + CH_3 \cdot COOH = 2HCl + \underset{\text{Cinnamic acid}}{C_6H_5 \cdot CH : CH \cdot COOH.}$$

Ethyl acetoacetate and also malic acid act on phenols in presence of concentrated sulphuric acid, giving anhydrides of unsaturated phenolic acids, *e.g.*

$$C_6H_4 \begin{cases} CH : CH \\ \quad\;\; | \\ O\text{---}CO \end{cases} \text{(}\textit{coumarin}\text{).}$$

(*a*) MONOBASIC AROMATIC ACIDS

The isomerism among these compounds is similar to that of the halogen derivatives of aromatic hydrocarbons.

BENZOIC ACID, $C_6H_5 \cdot COOH$, is found naturally in various resins (*e.g.* gum benzoin) and in balsam of Tolu, from which it is obtained by sublimation or by heating with milk of lime. It is formed in the urine of herbivorous animals as **Hippuric Acid**, which gives glycocoll and benzoic acid on putrefaction. It forms white leaflets melting at 121° and boils at 250°; it sublimes at 100° to 120° and distils in steam. It has an irritating odour and is soluble in boiling water; its alkali salts crystallise well ($C_6H_5 \cdot CO_2K + \frac{1}{2}H_2O$) and dissolve in water.

It is prepared industrially by converting toluene (from light tar oils), by means of chlorine, into benzenyl trichloride, $C_6H_5 \cdot CCl_3$, and heating this with milk of lime under pressure: $2C_6H_5 \cdot CCl_3 + 4Ca(OH)_2 = 3CaCl_2 + (C_6H_5 \cdot COO)_2Ca + 4H_2O$ (with traces of chlorobenzoic acid). Instead of being treated with lime, the benzenyl trichloride may be oxidised directly with dilute nitric acid, in vessels fitted with stirrers, as long as hydrogen chloride is evolved, the benzoic acid being then distilled, allowed to crystallise, centri-

MONOBASIC AROMATIC ACIDS

Formula	Name	Position of the groups	Melting-point
$C_6H_5\cdot CO_2H$	Benzoic (benzenecarboxylic)	—	121°
$CH_3\cdot C_6H_4\cdot CO_2H$	o-Toluic (o-methylbenzenecarboxylic)	1 : 2	105°
”	m- ” (m- ”)	1 : 3	111°
”	p- ” (p- ”)	1 : 4	179°
$C_6H_5\cdot CH_2\cdot CO_2H$	Phenylacetic	—	76°
$C_6H_3(CH_3)_2\cdot CO_2H$	Hemellitic	1 · 2-3	144°
”	o-Xylic (1-CH_3 ; 2-CH_3, 4-CO_2H)	1 · 2-4	166°
”	m- ” (*vic*)	1 : 3-2	98°
”	m- ” (*as*)	1 · 3-4	126°
”	Mesitylenic	1 · 3-5	166°
”	p-Xylic	1 : 4-2	132°
$C_6H_5\cdot CH_2\cdot CH_2\cdot CO_2H$	Hydrocinnamic	—	49°
$C_6H_5\cdot CH(CH_3)\cdot CO_2H$	Hydratropic (methylphenylacetic)	—	below − 20° (b.pt 267°)
$C_2H_5\cdot C_6H_4\cdot CO_2H$	o-Ethylbenzoic	1 : 2	68°
”	p- ”	1 : 4	112°
$C_6H_2(CH_3)_3\cdot CO_2H$	Prehnitylic (trimethylbenzenecarboxylic)	1 · 2 · 3-4	168°
”	α-Isodurylic ”	1 . 2 · 3-5	215°
”	Durylic ”	1 : 2 : 4-5	149°
”	γ-Isodurylic ”	1 : 2 : 4-6	127°
”	Mesitylenecarboxylic ”	1 : 3 . 5-2	152°
$C_3H_7\cdot C_6H_4\cdot CO_2H$	Cuminic (p-isopropylbenzoic)	1 : 4	117°
$C_6H(CH_3)_4\cdot CO_2H$	Prehnitenecarboxylic (tetramethylbenzoic)	1 · 2 3 . 4-5	165°
”	Isodurenecarboxylic ”	1 : 2 : 3 : 5-4	161°
”	Durenecarboxylic ”	1 : 2 . 4 : 5-3	179°
$C_6(CH_3)_5\cdot CO_2H$	Pentamethylbenzoic	1 : 2 : 3 : 4 : 5 : 6	210·5°
$C_6H_5\cdot CH : CH\cdot CO_2H$	Cinnamic	—	133° (b.pt. 300°)
$C_6H_5\cdot C(: CH_2)\cdot CO_2H$	Atropic	—	107° (b.pt. 267°)
$C_6H_5\cdot C \vdots C\cdot CO_2H$	Phenylpropiolic	—	137°
$OH\cdot C_6H_4\cdot CH : CH\cdot CO_2H$	o-Coumaric	1 . 2	208°
”	p- ”	1 : 4	206°
$OH\cdot C_6H_4\cdot CO_2H$	o-Hydroxybenzoic (salicylic)	1 : 2	159°
”	m- ” ”	1 . 3	200°
”	p- ” ”	1 : 4	210°
$CH_3O\cdot C_6H_4\cdot CO_2H$	Anisic	1 · 4	184°
$CH_3\cdot C_6H_3(OH)\cdot CO_2H$	o-Hydroxytoluic	1 : 2-3	164°
”	m- ”	1 : 3-4	177°
”	p- ”	1 : 4-3	151°
”	β-m- ”	1 : 3-2	168°
$OH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CO_2H$	Hydro-p-coumaric	1 · 4	118°
$C_6H_5\cdot CH(OH)\cdot CO_2H$	Mandelic	—	118°
$C_6H_5\cdot CH(CH_2\cdot OH)\cdot CO_2H$	Tropic	—	117°
$C_6H_5\cdot CO\cdot CO_2H$	Benzoylformic	—	65°
$C_6H_5\cdot CO\cdot CH_2\cdot CO_2H$	Benzoylacetic	—	103°
$C_6H_3(OH)_2\cdot CO_2H$	Protocatechuic	1 : 3-4	199°
$C_6H_2(CH_3)(OH)_2\cdot CO_2H$	Orsellinic (1-methyl-3 : 5-dihydroxybenzene -2-carboxylic	1 : 3 : 5-2	176°
$C_6H_2(OH)_3\cdot CO_2H$	Gallic (3 : 4 . 5-trihydroxybenzenecarboxylic	3 : 4 . 5-1	221°

fuged, and purified by sublimation. Jessnitzer (Ger. Pat. 236,489 of 1910) proposes to oxidise with calcium hypochlorite instead of with nitric acid.

Benzonitrile, $C_6H_5\cdot CN$, found in the middle tar oils, gives pure benzoic acid when hydrolysed (Ger. Pat. 109,122).

According to Ger. Pat. 136,410, benzoic and phthalic acids are readily obtainable by heating naphthol or other naphthalene derivative with fused or dissolved alkali in presence of metallic oxides (MnO_2, CuO, Fe_2O_3) ; the benzoic acid is separated from the mixture by distillation.

Benzoic acid is used in medicine, in making certain aniline blues, in the seasoning of tobacco, in printing textiles, and for preserving foodstuffs,[1] although it has not been shown to be harmless when used in this way ; experiments made in the United States in 1910 showed that doses of 1 grm. per

[1] Of the various methods for detecting benzoic acid in foods, the following may be mentioned. According to Jonescu (1909) the presence of benzoic acid in *milk* may be shown by converting it into *salicylic acid* by means of 3 per cent. hydrogen peroxide diluted ten times, and then testing for salicylic acid with ferric chloride solution (sp. gr. 1·28) diluted ten times (as in the examination of beer, *see* p. 179). In the case of *butter*, this is acidified with sulphuric acid and distilled with steam, the distillate being tested as above (*see also* Salicylic Acid).

day of benzoic acid or sodium benzoate have no injurious effect. It costs about 3*s*. to 4*s*. per kilo.

BENZOIC ANHYDRIDE, $(C_6H_5\cdot CO)_2O$, is obtained by heating an alkali benzoate with benzoyl chloride:

$$C_6H_5\cdot CO_2Na + C_6H_5\cdot CO\cdot Cl = NaCl + (C_6H_5\cdot CO)_2O,$$

or, according to Ger. Pat. 146,690, by heating nearly 2 parts of sodium chlorosulphonate, $Cl\cdot SO_3Na$, with 3 parts of sodium benzoate; by changing these proportions, benzoyl chloride (*see below*) may be obtained.

In the cold it is not decomposed by water, but on boiling it gives benzoic acid. It costs 16*s*. to 20*s*. per kilo according to its purity.

BENZOYL CHLORIDE, $C_6H_5\cdot CO\cdot Cl$, is formed by the action of PCl_5 or $POCl_3$ on benzoic acid, and is obtained industrially either by the action of chlorine on benzaldehyde or from sodium chlorosulphonate (*see above*, Benzoic Anhydride). It is a colourless liquid which boils at 194°, and has a very pungent odour. Water decomposes it very slowly in the cold (distinction from acetyl chloride) giving hydrochloric and benzoic acids. It reacts readily with many compounds in alkaline solution, introducing into them the benzoyl group (Schotten and Baumann's method). For instance, a mixture of benzoyl chloride with a little potassium hydroxide acts in the cold on aniline, forming **Benzanilide**, $C_6H_5\cdot NH\cdot CO\cdot C_6H_5$ (white compound, melting at 158°, and boiling unaltered). With hydroxylamine it gives **Benzhydroxamic Acid**, $C_6H_5\cdot CO\cdot NH\cdot OH$, which gives a violet coloration with ferric chloride.

Benzoyl chloride is used in the preparation of benzaldehyde and of various dyes; it costs about 5*s*. 6*d*. per kilo, or, in the highly purified state, 16*s*.

ETHYL BENZOATE, $C_6H_5\cdot CO_2C_2H_5$, has an odour of mint, and is obtained by heating benzoic acid with alcohol in presence of sulphuric acid.

BENZAMIDE, $C_6H_5\cdot CO\cdot NH_2$, is obtained by the action of ammonia (or ammonium carbonate) on benzoyl chloride, or by the interaction of sulphuric acid and benzonitrile. It forms nacreous crystals melting at 130°, and is soluble in boiling water. It forms metallic derivatives more easily than acetamide.

BENZHYDRAZIDE, $C_6H_5\cdot CO\cdot NH\cdot NH_2$, is obtained from hydrazine hydrate and benzoic ester; with nitrous acid, it gives

BENZAZIDE (**Benzoylazoimide**), $C_6H_5\cdot CO\cdot N\langle{}^{N}_{N}\rangle\!\!\|$, which is readily hydrolysed, giving hydrazoic and benzoic acids.

HIPPURIC ACID, $C_6H_5\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, is obtained by heating benzoic acid with glycocoll. It occurs in the urine after ingestion of benzoic acid or toluene, and is found in considerable quantities in the urine of horses and other herbivorous animals. It forms rhombic crystals melting at 187°, and is soluble in hot water.

CHLOROBENZOIC ACIDS, $C_6H_4Cl\cdot CO_2H$. The halogen enters preferably the meta-position and nitric acid (in presence of concentrated sulphuric acid) gives mainly **m-Nitrobenzoic Acid**, $NO_2\cdot C_6H_4\cdot CO_2H$, which, on reduction, yields **Azobenzoic Acids** and **Aminobenzoic Acids**, $NH_2\cdot C_6H_4\cdot CO_2H$. The latter, like glycine, exhibit the functions of both acids and bases; with nitrous acid, they form **Diazobenzoic Acids**, $C_6H_4\langle{}^{N:N}_{CO_2}\rangle$.

ANTHRANILIC ACID (**o-Aminobenzoic Acid**) is formed in the synthesis of indigo and also from phthalimide. It is prepared by boiling the potassium derivative of phthalylhydroxylamine with aqueous sodium carbonate:

$$C_6H_4\langle{}^{CO}_{CO}\rangle N\cdot OH + H_2O = CO_2 + C_6H_4\langle{}^{NH_2}_{CO_2H}.$$

Numerous patents have been taken out for its manufacture (Ger. Pats. 130,302, 136,788, 138,188, 145,604, 146,716, &c.). It melts at 145°, and is largely used in the manufacture of dyes, drugs, and perfumes. The pure product costs 64*s*. and the crude 20*s*. per kilo.

Anthranilic acid forms an internal anhydride, **Anthranil**, $C_6H_4\langle{}^{CO}_{NH}\rangle\!|$.

Of the dibasic **Sulphobenzoic Acids**, $C_6H_4(SO_3H)(CO_2H)$, the ortho-isomeride is of interest, since its imino-derivative forms **SACCHARIN** (**o-Benzoicsulphimide**), $C_6H_4<\substack{SO_2\\CO}>NH$, which is a white powder slightly soluble in water, and is 500 times as sweet as sugar. Saccharin is prepared as follows: toluene is heated at 100° with concentrated sulphuric acid and the mixture of o- and p-toluenemonosulphonic acids thus obtained converted into calcium salt and thence into sodium salt. This is dried and distilled in presence of phosphorus trichloride and chlorine and the o- and p-toluenesulphonic chlorides frozen and centrifuged to separate the crystalline para-compound from the liquid ortho-compound. With ammonia, the latter gives o-toluene-sulphamide, which is oxidised by permanganate to the potassium salt of o-benzene-sulphammic acid and treatment of this with an acid results in the separation of crystals of saccharin. It has no nutritive value, but is harmless in the amounts usually introduced into foods; in large doses, it is antiseptic, antifermentative, and diuretic. It melts at 224°. In Italy its consumption is prohibited, for fiscal reasons. It costs 40*s*. to 48*s*. per kilo. With alkali carbonates it forms *soluble saccharin* (*crystallose*).

Saccharin was discovered in 1878, and in 1896 there were three factories in Germany producing 33,528 kilos; in 1897 four factories made 34,682 kilos; in 1898 five factories made 78,363 kilos and in 1899 six factories 130,287 kilos; in 1901 189,734 kilos were made, and in 1902 174,777. Its sale is now prohibited in Germany, but six firms in Switzerland produce annually about 80,000 kilos which they despatch as contraband to various countries. In 1908 a fine of nearly £25,000 was inflicted at Domodossola for the smuggling of 623 kilos of saccharin. A pharmacist in Hungary was found in 1908 to have sold saccharin illegally to the value of £20,000.

In Russia 56,332 kilos were imported in 1899 when its consumption was allowed, but after its importation was prohibited it fell to 831 kilos in 1906, although a considerable amount is introduced without the knowledge of the Customs authorities. An International Convention at Brussels in 1909 passed a resolution that all countries should prohibit the use of saccharin in foods and beverages and placed severe restrictions on its sale.

TOLUIC ACIDS, $CH_3 \cdot C_6H_4 \cdot COOH$. The three isomerides are obtained by oxidising the corresponding xylenes with dilute nitric acid (*see* Table, p. 577). p-Toluic acid is formed also by the oxidation of turpentine.

Phenylacetic Acid (*α-Toluic acid*), $C_6H_5 \cdot CH_2 \cdot CO_2H$, is isomeric with the toluic acids, but it gives benzoic acid on oxidation, whereas the toluic acids give *phthalic acids*.

XYLIC ACIDS, $C_6H_3(CH_3)_2 \cdot CO_2H$; various isomerides are known (*see* Table, p. 577).

CUMINIC ACID (*p*-**Isopropylbenzoic Acid**), $C_3H_7 \cdot C_6H_4 \cdot CO_2H$, is formed in animal organisms by the oxidation of cymene, and is obtained by oxidation of Roman chamomile oil with permanganate. It melts at 117° and yields cumene when distilled with lime.

CINNAMIC ACID, $C_6H_5 \cdot CH : CH \cdot CO_2H$, is found in storax and in certain balsams (Tolu, Peru, &c.), and remains as sodium salt when these are distilled with caustic soda. It is prepared according to Perkin's synthesis (p. 291) by heating benzaldehyde with sodium acetate in presence of a dehydrating agent (acetic anhydride); or by heating benzylidene chloride (benzal chloride) with sodium acetate in an autoclave at 200°; or by the malonic synthesis from benzaldehyde and ammonia:

$$C_6H_5 \cdot CHO + CH_2(COOH)_2 = H_2O + CO_2 + C_6H_5 \cdot CH : CH \cdot COOH.$$

Cinnamic acid melts at 133° and boils at about 300°. It readily forms additive products owing to the double linking in the side-chain, and on this account also reduces permanganate in presence of sodium carbonate (Baeyer's reaction, p. 88).

According to theory, the presence of the double linking should result in the existence of two stereoisomerides :

$$\begin{array}{c} C_6H_5\cdot C\cdot H \\ \| \\ H\cdot C\cdot CO_2H \end{array} \quad \text{and} \quad \begin{array}{c} C_6H_5\cdot C\cdot H \\ \| \\ CO_2H\cdot C\cdot H \end{array}$$

But, in addition to these, two others, **Allocinnamic** and **Isocinnamic Acids**, are known and are apparently polymorphous modifications of the maleic form, although this question—studied by Liebermann, Michael, and Erlenmeyer, jun.—has not yet been completely decided.

Cinnamic acid costs 16*s*. per kilo, and is used in medicine and in the synthesis of various perfumes.

PHENYLPROPIOLIC ACID, $C_6H_5\cdot C \vdots C\cdot CO_2H$, is obtained by heating the dibromide of ethyl cinnamate with alcoholic potash:

$$C_6H_5\cdot CHBr\cdot CHBr\cdot CO_2C_2H_5 + H_2O = 2HBr + C_6H_5\cdot C \vdots C\cdot CO_2H + C_2H_5\cdot OH.$$

It forms shining needles which melt at 137° and readily sublime. Its sodum salt is used. n 1 to 3 per cent. solution as an inhalation in cases of tuberculosis, and costs £4 per kilo

o-**Nitrophenylpropiolic Acid,** obtained in a similar manner from ethyl o-nitrocinnamate, s used in the synthesis of indigo.

(*b*) DIBASIC AND POLYBASIC AROMATIC ACIDS

The basicity of these acids is given by the number of carboxyl groups, and the phenomena of isomerism are similar to those of the dihalogenated derivatives. The carboxyl groups may be united directly to the benzene nucleus or to side-chains, and by means of them esters, amides, acid chlorides, &c., can be formed.

PHTHALIC ACID (Phenylene-*o*-dicarboxylic Acid), $C_6H_4\!<\!\begin{smallmatrix}COOH(1)\\COOH(2)\end{smallmatrix}$, is obtained by oxidising compounds with two lateral chains, but not by chromic acid, which would partially destroy the benzene nucleus.

At one time it was prepared industrially by chlorinating naphthalene and then oxidising (Laurent). But since a few years ago it has been obtained more conveniently by oxidising naphthalene with fuming sulphuric acid in presence of mercury salts or, better, rare earth salts (thorium, &c.), which act as catalysts.

This catalytic process, which is due to Sapper, allows of the recovery of the whole of the mercury, while the sulphur dioxide evolved is converted again into sulphur trioxide, so that the oxidation of the naphthalene may be regarded as taking place at the expense of the oxygen of the air. This economical process has rendered possible the industrial preparation of artificial indigo.

The process of fusing naphthols with alkali in presence of metallic oxides also seems to give good results and yields benzoic acid at the same time (*see above*). According to Ger. Pat. 152,063, the electrolysis of naphthalene in presence of an acid solution of a cerium compound yields naphthaquinone and phthalic acid.

It is a white, crystalline substance soluble in hot water, alcohol, and ether. It melts at 213° and is then transformed into **Phthalic Anhydride,** $C_6H_4\!<\!\begin{smallmatrix}CO\\CO\end{smallmatrix}\!>\!O$, which melts at 128° and boils at 277°, but sublimes considerably below this temperature ; the anhydride has a characteristic odour and gives phthalic acid when boiled with water.

With PCl_5, phthalic acid gives **Phthalyl Chloride,** $C_6H_4\!<\!\begin{smallmatrix}CCl_2\\CO\end{smallmatrix}\!>\!O$, which gives **Phthalide,** $C_6H_4\!<\!\begin{smallmatrix}CH_2\\CO\end{smallmatrix}\!>\!O$, on reduction, and **Phthalophenone,** $C_6H_4\!<\!\begin{smallmatrix}C(C_6H_5)_2\\CO\end{smallmatrix}\!>\!O$, with benzene (+ $AlCl_3$).

When heated with phenols and sulphuric acid, phthalic anhydride forms *phthaleins, e.g.*

$$C_6H_4{<}^{CO}_{CO}{>}O + 2C_6H_5\cdot OH = H_2O + C_6H_4{<}^{C(C_6H_4\cdot OH)_2}_{CO}{>}O \text{ (phenolphthalein).}$$

Phenolphthalein is a yellow powder and, being a phenol, dissolves in alkali, the solution having a violet-red colour (it forms an excellent indicator, *see* vol. i, p. 97). When heated with resorcinol in presence of zinc chloride at 210°, phthalic anhydride yields **Fluorescein** (*resorcinolphthalein*),

$$CO{<}^{C_6H_4}_{-\,O\,-}{>}C{<}^{C_6H_3(OH)}_{C_6H_3(OH)}{>}O,$$

which, even in very dilute alkaline solution, shows an intense greenish yellow fluorescence while by transmitted light the solution appears reddish (*see* Triphenylmethane Dyes).

Tetrabromofluorescein, or *eosin*, gives alkaline solutions showing a marked reddish green-yellow fluorescence, and is used for dyeing silk red, producing a beautiful fluorescent effect; the colour is, however, not very stable, especially towards light.

With dry ammonia in the hot, phthalic anhydride gives **Phthalimide**, $C_6H_4{<}^{CO}_{CO}{>}NH$, which is of importance since the iminic hydrogen can be replaced by metals and the latter under the action of alkyl halides, by alkyl groups. The compounds thus obtained, when heated with acid or alkali, yield phthalic acid and a *primary amine* free from secondary or tertiary amine (important general synthesis of primary amines, discovered by Gabriel):

$$C_6H_4{<}^{CO}_{CO}{>}NK + C_2H_5Br = KBr + C_6H_4{<}^{CO}_{CO}{>}NC_2H_5, \text{ and}$$

$$C_6H_4{<}^{CO}_{CO}{>}NC_2H_5 + 2H_2O = C_6H_4{<}^{CO_2H}_{CO_2H} + C_2H_5\cdot NH_2.$$

Phthalic acid is used in the synthesis of indigo and of dyes of the pyronine group, and is usually placed on the market as the anhydride (although called acid) at a price of £6 per quintal (65 per cent. strength); chemically pure, it costs 4*s*. per kilo.

ISOPHTHALIC ACID, $C_6H_4(CO_2H)_2(1:3)$, is obtained by oxidation of colophony with nitric acid, or, in general, by the oxidation of meta-derivatives of benzene. The barium salt is soluble in water.

TEREPHTHALIC ACID, $C_6H_4(CO_2H)_2(1:4)$, is formed by oxidising oil of turpentine or chamomile oil, or by oxidising p-toluic acid with permanganate. It is almost insoluble in water and alcohol and sublimes unchanged. It gives a sparingly soluble barium salt, but does not form an anhydride.

POLYBASIC ACIDS. The tri-, tetra-, penta-, and hexa-carboxylic acids are known, but are of little practical importance.

The **Benzenetricarboxylic Acids** are: **TRIMESIC ACID** (1 : 3 : 5) derived from mesitylene; **TRIMELLITIC ACID** (1 : 2 : 4) obtained from colophony; **HEMIMELLITIC ACID** (1 : 2 : 3).

The **Benzenetetracarboxylic Acids** are: **PYROMELLITIC ACID** (1 : 2 : 4 : 5), melting at 264°; **PREHNITIC ACID** (1 : 2 : 3 : 4), melting at 237° and forming an anhydride **Mellophanic Acid** (1 : 3 : 4 : 5), which melts, and is converted into anhydride, at 280°.

MELLITIC ACID (**Benzenehexacarboxylic Acid**), $C_6(COOH)_6$, is obtained from mellite, which is a kind of mineral found in deposits of lignite, and consists of yellow, quadratic octahedra of aluminium mellitate, $C_6(COO)_6Al_2 + 18H_2O$.

Mellitic acid may also be obtained by oxidising wood charcoal with alkaline permanganate. It forms needles insoluble in water and alcohol and, when heated, loses $2H_2O$ and $2CO_2$, forming **Pyromellitic Anhydride**, $O{<}^{\overset{1}{CO}}_{\underset{2}{CO}}{>}C_6H_2{<}^{\overset{4}{CO}}_{\underset{5}{CO}}{>}O$, which gives **Pyromellitic Acid**, $C_6H_2(CO_2H)_4$, with water.

Mellitic acid cannot form substitution products, since all the benzene hydrogens are already substituted, but on reduction with sodium amalgam it readily yields **Hydromellitic Acid**, $C_6H_6(COOH)_6$, which gives benzene when distilled with lime.

(c) HYDROXY-ACIDS AND PHENOLIC ACIDS

These are formed by the methods given on p. 575 or by oxidising homologues of phenol or fusing them with alkali. The basicity is given by the number of carboxyl and phenolic groups, both of these leading to salt-formation, but the basicity towards sodium carbonate is determined by the carboxyl groups alone. When both the carboxyl and hydroxyl groups are etherified, only the former can be subsequently hydrolysed.

SALICYLIC ACID (*o*-Hydroxybenzoic Acid), $OH \cdot C_6H_4 \cdot COOH$, is the most important of the hydroxy-acids. It is derived from *salicin* (glucoside of willow bark), which, when hydrolysed, first gives glucose and **Saligenin** :

$$\underset{\text{Salicin}}{C_6H_4{<}^{O \cdot C_6H_{11}O_5}_{CH_2 \cdot OH}} + H_2O = \underset{\text{Saligenin}}{C_6H_4{<}^{OH}_{CH_2 \cdot OH}} + \underset{\text{Glucose}}{C_6H_{12}O_6},$$

the saligenin giving salicylic acid on oxidation. The acid is found as methyl ester in the essence of *Gaultheria procumbens.*

It is prepared industrially by heating sodium phenoxide with carbon dioxide in an autoclave at 140°, according to Kolbe's process ; from the resulting sodium salicylate the acid is liberated by treatment with a mineral acid. In Marasse's method a mixture of phenol and potassium carbonate is heated in presence of CO_2 at 140° to 160°.

It forms white crystals melting at 156°, subliming at 200°, and distilling in superheated steam at 170°. It is readily soluble in alcohol or in ether, and 1 part dissolves in 444 parts of water at 15° and in 13 parts of hot water. When heated with $POCl_3$ it gives the **Internal Anhydride**, $C_6H_4{<}^{O}_{CO}{\Big|}$, which forms a white powder softening at 110° and melting at 261°.

With bromine water it gives a precipitate, $C_6H_2Br_3 \cdot OBr$, and with ferric chloride it gives a violet coloration even in alcoholic solution (phenol is coloured only in aqueous solution). With lime-water in the hot it forms a basic salt, $C_6H_4{<}^{-O-}_{COO}{>}Ca$, and can thus be separated from its isomerides, which do not give this reaction.

It is used as an antiseptic for preserving foodstuffs,[1] and in the manufacture of dyes and perfumes. Its sodium salt is largely used as a medicine.

When heated to 200° it loses CO_2, giving **Phenyl Salicylate** (*salol*) :

$$2OH \cdot C_6H_4 \cdot CO_2H = CO_2 + H_2O + OH \cdot C_6H_4 \cdot CO_2C_6H_5,$$

which is used as an antiseptic for the intestines.

Salicylic acid costs £12 14*s*. per quintal. In 1905 Germany exported 5018 quintals of the acid and its sodium salt.

Acetylsalicylic Acid is used in medicine under the name *aspirin.*

m and *p*-**HYDROXYBENZOIC ACIDS** give insoluble basic barium salts and yield no coloration with ferric chloride ; the m-acid is more stable to heat than the o- or p-acid.

Anisic Acid, $CH_3O \cdot C_6H_4 \cdot CO_2H$, resembles the monobasic acids more than the phenols and is obtained from p-hydroxybenzoic acid, methyl alcohol, potassium hydroxide, and methyl iodide, the dimethyl ether obtained being then partially hydrolysed.

Methyl Salicylate, $OH \cdot C_6H_4 \cdot CO_2CH_3$, forms 90 per cent. of oil of Gaultheria, and is prepared artificially by the interaction of salicylic acid (2 parts) and methyl alcohol (2 parts)

[1] The examination of foods for the presence of salicylic acid is carried out in the same way as with beer (p. 179). But baked starchy substances (bread, &c.) contain *maltol,* which gives the same reaction as salicylic acid and is, like the latter, volatile. In this case Jorissen's method must be used in testing for salicylic acid : 10 c.c. of the liquid distilled with steam are treated with 5 drops of 10 per cent. potassium nitrite solution, 5 drops of 50 per cent. acetic acid, and one drop of 10 per cent. copper sulphate solution. The liquid is then boiled and in presence of even less than 0 0001 grm of salicylic acid a reddish coloration forms, which rapidly becomes blood-red (H. C. Sherman, 1910).

in presence of concentrated sulphuric acid (1 part). It boils at 224°, is used as a perfume, and costs 3*s.* 6*d.* per kilo.

p-HYDROXYPHENYLACETIC ACID, $OH\cdot C_6H_4\cdot CH_2\cdot CO_2H$, formed during the putrefaction of proteins and occurring in the urine, gives a dirty green coloration with ferric chloride.

Of the Dihydroxybenzoic Acids, PROTOCATECHUIC ACID (3 : 4-Dihydroxybenzoic Acid), $C_6H_3(OH)_2\cdot CO_2H$, forms shining scales or crystals soluble in water; in solution it is coloured green by ferric chloride, the colour being changed to blue and then to red by a little soda. It can be obtained synthetically, together with the 2 : 3-dihydroxy-acid, by heating catechol with ammonium carbonate, and is prepared by fusing various resins with alkali. Like catechol, it exhibits reducing properties. Its monoethyl ether ($3OCH_3$) is VANILLIC ACID, which is formed by the oxidation of vanillin (p. 574); its dimethyl ether [$(OCH_3)_2$] is VERATRIC ACID, found in the seeds of *Veratrum Sabadilla;* and its Methylene Ether, $CO_2H\cdot C_6H_3{<}^{O}_{O}{>}CH_2$, is PIPERONYLIC ACID, which is also obtained by oxidising piperinic acid.

GALLIC ACID (3 : 4 : 5-Trihydroxybenzenecarboxylic Acid), $C_6H_2(OH)_3\cdot CO_2H$, occurs naturally as glucosides in various plants and in tea, gall-nuts, &c. It is formed by the action of mould on solutions of tannin or by boiling the latter with dilute acid or caustic soda.

It reduces gold and silver salts and becomes oxidised and turns brown in the air. With ferric chloride it gives a black coloration, and, on this account, it is used in making ink [1]; its reducing properties are utilised in photography.

When pure it forms colourless needles ($+ H_2O$) which decompose at 200° into carbon dioxide and pyrogallol. It is only slightly soluble in ether or cold water but dissolves readily in alcohol or hot water.

Chemically pure gallic acid costs about 5*s.* per kilo.

There are a number of *hydroxy-acids* with hydroxyl and carboxyl groups in the side-chains: mention may be made of:

(1) COUMARIC ACID (*o*-Hydroxycinnamic Acid), $OH\cdot C_6H_4\cdot CH : CH\cdot CO_2H$, which does not give an anhydride owing to its fumaroid structure (*see* Fumaric Acid), while the maleic stereoisomeride, Coumarinic Acid, is known only as salts, since in the free state it immediately forms Coumarin, $C_6H_4{<}\begin{matrix} O\text{---}CO \\ | \\ CH : CH \end{matrix}$; the latter may also be obtained by heating salicylic acid with sodium acetate (Perkin synthesis; *see* Aldehydes).

(2) MANDELIC ACID, $C_6H_5\cdot CH(OH)\cdot CO_2H$; of the various stereoisomerides, that occurring naturally is lævo-rotatory, while that obtained synthetically (from benzaldehyde and hydrocyanic acid, with subsequent hydrolysis) is the racemic form. In solutions of the latter, certain Schizomycetes destroy the d- and leave the l-isomeride, whilst *Penicillium*

[1] INK is made by adding to aqueous gallic acid or tannin ferrous sulphate solution slightly acidified with acetic or hydrochloric acid in order to prevent oxidation and the formation of a black precipitate. To this brownish solution is added a solution of indigo-carmine or logwood to render the writing visible. When the ink is exposed on the paper to the air, it becomes black and insoluble, owing to the evaporation or neutralisation of the acid by the sizing of the paper (albumen, &c.), and the consequent ready oxidation by atmospheric oxygen, which changes the original blue colour to a deep black.

To make the ink adhere without spreading, a little gum is added, and to preserve it, a little phenol [1 litre of this normal ink may be obtained from 23·4 grms. of tannin, 7·7 grms of gallic acid, 10 grms. of gum, 2·5 grms. of hydrochloric acid (as gas) or 7·5 grms. of the concentrated acid, 30 grms. of ferrous sulphate, 1 grm. of phenol, and the rest water; the liquid is left at rest for four days and then decanted from the deposit and coloured with indigo-carmine or logwood extract].

A *logwood ink* may be obtained as follows: 20 grms. of dry logwood extract or 30 grms. of the paste (hæmatein) are dissolved in 800 c.c. of water and to the hot solution are added 15 grms. of soda crystals (7 grms. of Solvay soda), and then, drop by drop, and with shaking, 100 c.c. of a solution containing 1 grm. of normal potassium chromate; this process gives a fine blue-black tint, and the ink, which does not attack steel pens, and dries easily can be preserved by a trace of phenol

Coloured inks are aqueous, gummy solutions of aniline dyes. Copying inks are similar to ordinary writing inks, but are more concentrated, and contain also glycerine, sugar, dextrin, calcium chloride, &c., by which the writing is kept moist for some time.

glaucum destroys the l- and leaves the d-compound. Also, if the cinchonine salt of the racemic form is prepared, the d-salt crystallises out first.

The **Dihydroxycinnamic Acids** include: **CAFFEIC ACID** [(*see* Chapter on Glucosides), **FERULIC ACID** and **UMBELLIC ACID** (p-hydroxy-o-coumaric acid, which is readily transformed into its anhydride, *umbelliferone*); a similar acid is **PIPERINIC ACID**,

$$CH_2{<}^{O}_{O}{>}C_6H_3\cdot CH:CH\cdot CH:CH\cdot CO_2H,$$

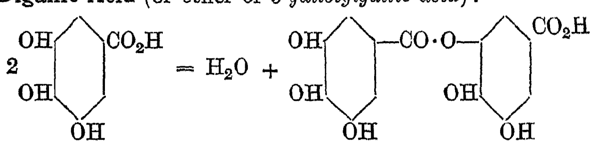
which is formed in the decomposition of piperine.

The derivatives of the **Trihydroxycinnamic Acids** are dealt with in the Chapter on Glucosides (*æsculin* and *daphnin* from horse chestnuts and *Daphne mezereum*, &c., respectively). Mention may be made here of **ÆSCULETIN** (a **Dihydroxycoumarin**),

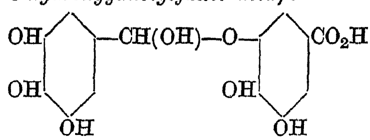
$$C_6H_2(OH)_2{<}\begin{matrix} O\cdot CO \\ | \\ CH:CH \end{matrix}$$

, and of the isomeric **DAPHNETIN**, which have also been obtained synthetically.

TANNIN (**Gallotannic** or **Tannic Acid**), $C_{14}H_{10}O_9$, was studied originally by Berzelius, Pelouze, and Liebig. According to Hlasiwetz (1867) and to U. Schiff (1873), tannin is probably a partial and mixed anhydride of gallic acid, 2 mols. of which are condensed with loss of 1 mol. of water from a carboxyl and a hydroxyl group and formation of a **Digallic Acid** (or ether of 3-*gallolylgallic acid*):



According to the investigations of Nierenstein (1908) on the acetyl-derivatives and hydrolysis, commercial tannin would seem to be a mixture of digallic acid and **Leucotannin** (or ether of 3-*hydroxygallolylgallic acid*):



There appear, however, to be various more or less highly polymerised tannins with widely varying molecular weights. Some uncertainty still prevails as to the true molecular magnitude of tannin. Paternò (1907), from a study of the colloidal solutions, arrived at molecular weights varying from 430 to 470 (*i.e.* C_{21} . . . .), while Walden (1898), by the ebullioscopic method, obtained numbers between 760 (about C_{35} . . . .) and 1560 (about C_{70} . . . .), which are sharply distinguished from that of digallic acid (332). P. Biginelli (1911), on the basis of the property shown by tannin of forming additive products with water, alcohol and ether [*e.g.* $C_{41}H_{32}O_{25}$, $C_4H_{10}O$ (ether), which is stable even in a vacuum and is analogous to the oily compound, $C_{41}H_{32}O_{25}$, $6C_4H_{10}O$, $7H_2O$, previously obtained by Pelouze, and to others of Biginelli's compounds, namely, $C_{41}H_{32}O_{25}$, $6C_4H_{10}O$; $C_{41}H_{32}O_{25}$, $6C_2H_5\cdot OH$, and $C_{41}H_{32}O_{25}$, $5H_2O$], and also on the loss of CO_2 and H_2O with formation of **Hexahydroxybenzophenone**, $C_{13}H_{10}O_7$, when tannin is heated in aqueous solution with lead dioxide (the CO_2 liberated was estimated), holds that tannin has the formula $C_{41}H_{32}O_{25}$, and that it is probably a glucoside. It was, indeed, observed by Liebig and also by Hlasiwetz that when tannin is boiled with dilute sulphuric acid it decomposes into gallic acid and dextrin or gum (reacting with $6H_2O$); but Etti (1884) and Löwe found that tannin purified with ethyl acetate does not yield saccharine substances (dextrin, &c.).

Tannin is widespread in nature and occurs in abundance in *sumac* (*Rhus coriaria*), gall-nuts and oak-galls, which are pathological excrescences caused by incision of the oak branches by insects. To extract the tannin, the gall-nuts are ground to a coarse powder, which is treated in a battery of diffusors similar to those used for extracting beet-sugar (*see* p. 451). The crude aqueous solution of tannin thus obtained is filtered through a battery of filters and extracted,

in a closed copper vessel fitted with a stirrer, with crude ether (aqueous or not free from alcohol). After the liquid has been left at rest in vats for 8 to 10 days, the dense lower layer containing the tannin is decanted and freed from ether by distillation. The evaporation of the water present is effected in heated, rapidly rotating drums, or on zinc plates placed in desiccators. The dry mass is then subjected to short and gentle treatment with steam—a very soft, pale, ethereal tannin being thus obtained. Tannin solutions are also concentrated under reduced pressure in multiple-effect apparatus (*see* Sugar, p. 461).

Aqueous or **Alcoholic Tannin**, which is extracted by water or alcohol without being purified by means of ether, is less pure.

Pure tannin forms a pale yellow light powder or sometimes crystals. It is darkened in colour by light, turns brown in the air, and dissolves in its own weight of water, double its weight of alcohol or eight times its weight of glycerol or ethyl acetate. It is almost insoluble in ether, benzene, chloroform, petroleum ether or carbon disulphide. With iron salts it forms a bluish black precipitate and with albumin or starch, a gelatinous precipitate. In aqueous solution it is dextro-rotatory (+ 15° to + 20°).

According to the degree of purity, it costs from £10 to £14 per quintal, and it is used mainly, in conjunction with antimony salts, as a mordant in the dyeing of cotton with basic dyes. It is employed also in making ink and, along with gelatine, in clarifying beer and wine, forming with the gelatine a gummy precipitate which gradually settles and carries down with it the suspended matter of the liquid.

In 1905 Germany exported 7040 quintals of pure tannin of the value £80,000, while in 1909 the exports were 8135 and the imports 772 quintals.

In 1908 Turkey produced 70,000 tons of *valonia* (*Quercus ægilops*), the harvesting of which employs 70,000 workpeople.

The United States consumed in 1909 different tanning materials to the value of £4,200,000.

Imports into England amounted to:

	1910	1911
Tanning extracts	£749,410	£739,329
Tanning barks	225,642	243,128
Myrobolams	225,168	138,844
Sumac	105,620	103,981
Valonia	169,948	121,227
Gall-nuts	37,329	—

Powdered barks or woods are used, either before or after extraction, in tanning hides.

These *tannin extracts* [from oak bark (containing 10 to 20 per cent. of tannin), *mimosa* (30 per cent.), leaves and twigs of *sumac* (15 to 30 per cent.), *valonia* (20 to 45 per cent.), *Asiatic gall-nuts* (55 to 75 per cent.), *European gall-nuts* (25 to 30 per cent.), *divi-divi* (40 per cent.), *myrobolams* (30 per cent.), *quebracho wood* (22 per cent.), *horse-chestnut bark* (2 to 3 per cent.), *catechu* or *cutch* (40 or 50 per cent.), &c.], are now rationally prepared on an enormous scale by extracting the finely divided material with hot water in batteries of diffusors. The dilute solutions (1·5° to 3° Bé.) are filtered and then concentrated in a triple-effect vacuum evaporator (*see* p. 461) to the density 25°–30° Bé. For some years, however, certain extracts have been clarified or partially decolorised with alkali sulphite, bisulphite, or hydrosulphite (patented by Lepetit, Dollfus and Gansser, 1896) before concentration. The bisulphite renders the extracts much more soluble, as it converts part of the tannin substances into soluble sulphonic compounds, while in the resinous extract of quebracho it also causes decomposition of a glucoside present, giving the product the property of imparting a yellow colour to skins with an aniline mordant. Decoloration is, however, due more especially to the hydrosulphite either added directly (Lepetit's patent) or produced by reduction of the bisulphite added to the extract (1) by zinc or aluminium dust (Eng. Pat. 11,502 of 1902); (2) by treating the crude extract with aluminium sulphate and sodium bisulphate and then heating under pressure at 120°–130° (U.S. Pat. 740,283); (3) by treating the extract with a mixture of formaldehyde-bisulphite and formaldehyde-sulphoxylate (Fr. Pat. 362,780); or (4) according to the recent patent of L. Dufour (Genoa), by reducing the sulphite with thiosulphate, and then with formaldehyde. Use has also been made of the waste sulphite liquors from the manufacture of cellulose

(Ger. Pat. 132,224 and 152,236 ; U.S. Pat. 909,343, January 1909), of aluminium amalgam (Ger. Pat. 220,021), and of chromous salts (chloride, sulphate, acetate, &c.)

An interesting method of clarifying quebracho extract and rendering it soluble even in the cold is that of A. Redlich, L. Pollak, and C. Jurenka (Ger. Pat. 212,876 of 1908) : The paste deposited from the crude, cooled extract is shaken for six to seven hours with 1 part per thousand of soda at 50° to 100°, 50 litres of the red solution thus obtained being mixed with 1000 litres of the crude extract previously decanted and the whole left to stand. A flocculent deposit is thus obtained and a pale solution of pure extract which is decanted off and can be concentrated ; the flocculent precipitate can be dissolved again in dilute soda and used to clarify further quantities of crude extract. Any excess of red, alkaline solution may be employed for clarifying extracts of sumac, &c.

The price of tanning extracts is roughly proportional to their content of tannin or tannin substances,[1] which may vary from 20 per cent. to 50 per cent., but for a given content of tannin, extracts rich in red or orange colouring-matters have the greater value ; these matters are estimated in special colorimeters or in the spectroscope. A. Gansser has recently (1909) suggested the replacement of the direct test on hide by one on strips of animalised cotton (the latter being immersed in a bath of gelatine and then in one of formaldehyde) ; the resultant colour on the textile is similar to that obtained on hides.

In 1905 Germany imported 58,000 quintals of sumac (£40,550), 139,054 quintals of quebracho extract (£257,250), and 126,315 tons of quebracho wood (£600,000), 145,000 quintals of quebracho extract (£254,800) being exported.

The chestnut extract produced in Corsica amounted to 22,032 tons in 1906, to 18,275 tons in 1907 (the diminution being due to strikes), and to 25,000 tons in 1909.

The United States consumed about 70,000 tons of solid quebracho extract in 1908.

For the manufacture of tannin extracts (*e.g.* from chestnut wood) to pay, at least 300 quintals of wood must be treated per day ; the plant costs over £8000.

TANNING OF HIDES. The hides of oxen, horses, sheep, &c., even when freed from hair and flesh (*i.e.* in the form of *corium*), do not keep and readily putrefy during drying or in presence of moisture. When dressed (this was carried out as early as 2000 B.C.), and, more especially, when tanned, the hides are more tenacious and resistant, do not putrefy, and do not gelatinise with boiling water, since the fibres on which the tanning material is fixed (to the extent of 30 per cent. or even more) do not agglutinate during drying, and hence remain fibrous and do not become compact and horny. The *corium* or *derma*, *i.e.* the fibrous substance of the skin, is converted by tanning into *leather*.[2] Rational

[1] **ANALYSIS OF TANNING MATERIALS.** A solution is prepared containing not more than 0·6 to 0·8 grm. of dry residue per litre ; for this purpose 9 to 10 grms. of solid extract or 15 to 20 grms. of liquid extract are dissolved in a litre of tepid water. Of the various analytical methods, the least inexact is that of Procter, which was accepted by the International Congress of Leather-Trades Chemists at Turin, 1904. The amount of *total soluble substances* is determined, the difference between this and the *non-tannins* (not fixed by powdered hide) giving the tannins.

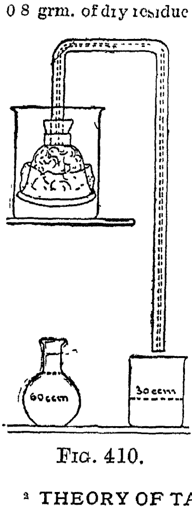


FIG. 410.

The *total soluble substances* are determined by evaporating 100 c.c. of the *clear*, filtered solution to dryness, and drying the residue at 100° to 105° until of constant weight.

Non-tannins. Powdered hide of the best quality is employed. With this is filled a glass bell or funnel (Fig. 410), holding about 30 c.c. and 3·5 cm. high and 3 cm. wide; the funnel is fitted with a rubber stopper, through which passes a capillary glass tube (2 mm. diameter) bent in the form of a syphon. The short limb of the tube penetrates 1 cm. below the stopper, and its end is surrounded with cotton- or glass-wool to retain the hide. The funnel holds about 7 grms. (not less than 5) of slightly compressed powdered hide, and the mouth of the funnel is closed by well-washed muslin tied tightly on. The funnel is arranged almost on the bottom of a 200 c.c. beaker, containing a little of the filtered tannin solution, and is left for an hour so that the hide powder may become moistened uniformly. The beaker is then filled with the tannin solution and suction applied to the long limb of the syphon (about 20 cm. longer than the short limb) so that about 90 to 100 c.c. flows out in 1·5 to 2 hours. The first 30 c.c. or so of the filtrate is discarded—until, indeed, a small portion fails to give a turbidity with the liquid obtained by treating 2 grms. of the hide powder with 60 c.c. of distilled water and filtering. Of the clear liquid free from tannin substances, 50 c.c. are evaporated in a platinum dish and the residue dried at 100° to 105°, until of constant weight. This weight is multiplied by 2 and subtracted from the total soluble substances (*see above*).

[2] **THEORY OF TANNING.** In the first half of last century, Davy, Séguin, Dumas, and Berzelius regarded the absorption of tannin by hides as a chemical reaction. In 1858 Knapp defined *leather* as an animal skin the fibres of which do not adhere during drying owing to the pores separating the fibres being filled with the tannin ; tanning would hence be a simple physical phenomenon. Similar views were expressed by Reiner (1872), Heinzerling (1882), Schroder and Passler (1892).

Th. Korner (1898–1903) also regarded it as a physical process, since neither the tanning material nor the fibres constituting the hides are electrolytically dissociated, and therefore cannot combine to form a kind of salt. Herzog, Adler, and Wislicenus (1904) also supported the physical theory.

tanning was introduced only when the anatomical structure of the skin became exactly known and the effects of tanning materials on the different parts of the hide were studied.

Various methods of tanning are in use: (*a*) **Mineral Tanning** or *tawing*, by means of alum and sodium chloride; (*b*) **Oil Tanning** or *chamoising*, with fatty materials; (*c*) **Ordinary Tanning** with tannin substances; (*d*) **Chrome Tanning**, using chromium salts (tanning with formaldehyde, proposed by Trillat and Payne; with quinone by Meunier and Seyewetz; with naphthols by Weinschenck; with rare earths by Garelli; with fatty acids by Knapp, or with the corresponding ammonium soaps by Garelli and Corridi, 1909.)

The preparation of the skins for tanning (swelling, unhairing, &c.) is carried out as described below under ordinary tanning.

(1) **Mineral Tanning** or *tawing* is frequently used for light lamb, sheep, and goat skins, which, after unhairing (*see later*), are passed into the limes and are then, just as in ordinary tanning, swelled in an acid bath, which also removes all the lime. They are then placed in the tanning vat containing alum or sodium chloride solution, without impregnating them with fatty substances. For twenty hides, about 1500 grm. of alum and 500 grm. of sodium chloride are dissolved in 50 litres of tepid water. The hides are well saturated with this bath and are heaped up still wet for two or three days, after which they are pressed, washed, and allowed to dry in the air.

The finishing of the tanned hides is carried out as described later.

As it has been established that the hide is capable of absorbing at its surface like a colloidal solution, Stiassny (1908) holds that tanning consists simply of a physical *absorption*, since tannin reacts with scarcely any of the known hydrolytic products of hides. Just as colouring-matters are fixed by carbon, silica, and alumina without there being any special groups to effect combination, so also in tanning all the known phenomena support the physical absorption hypothesis

According to Stiassny, every tanning process consists in the *absorption* of a dissolved colloidal substance by the gel of the hide and in simultaneous secondary transformations (polymerisations, oxidations, &c), to which the absorbed matter is subjected by the catalytic action of the hide, and which render the absorbed tannin insoluble and the process irreversible. This is more a physico-chemical than a physical theory.

Konnstein (Vienna) also regards the phenomena as a physical one, owing to the absence of stoicheiometric relations.

On the other hand, Muntz (1870) and Schroener (1890) hold that tanning must be due to a chemical phenomenon, since the same hide always absorbs the same maximum amount of a given tanning material, but Schroder and Passler advance the objection that below the limit of maximum absorption, the quantity fixed varies with the concentration of the bath, there being no stoicheiometric relations characteristic of chemical combination

Suida, Gelmo, and Fahrion (1903–1908) revert to the chemical theory, and assert that, as tanning is preceded by treatment with acid or mordant, slight dissociation or hydrolysis may occur (as in the case in the dyeing of wool) Further, hide powder fixes substantive dyes better than wool itself, and that the combination does not exhibit stoicheiometric proportions is explained by the fact that the hide consists of compact fibres and not of separate molecules as in solution, so that the tanning liquor penetrates only slowly into the interior of the mass, and is gradually impoverished and exhausted.

Fahrion (1908–1910) points out that in tanning with formaldehyde there can be no question of colloidal material (as with tannin), and with regard to the elimination of alum or tannin from leather by the mere action of water, this is due to *pseudo-tanning*, *i.e.* to the formation of labile, readily hydrolysable compounds, the tannin of which becomes distributed between the hide and the water. With reference to the non-stoicheiometric relations, he observes that the fixation of more tannin from concentrated than from dilute solutions is in accord with the law of mass action for reversible chemical reactions.

According to Heidenhain, Zacharias, and Fahrion (1908), both the dyeing and the tanning process occur in two phases, the absorption and penetration of the tanning substance and the subsequent chemical combination of this substance with the hide Garelli (1907–1910), from the results of his tanning experiments with rare earths (ceria, thoria, zirconia), supports this theory, and holds that all substances which in aqueous solution can undergo hydrolysis forming basic hydroxides or salts (like chromium, iron, and aluminium salts) are capable of tanning hides (*i.e.* the hide hydrolyses and decomposes the salts, which thus deposit hydrates or basic salts on the fibres of the *corium* or *derma*, the fibres and the salts combining to form leather). Thus, Garelli effected tanning with the rare earths, *i.e* with compounds of the trivalent (cerium, lanthanum, and didymium) or tetravalent elements (cerium, thorium, and zirconium; Zacharias had used stannic salts in 1903), and the tanning, as when alum is used, is facilitated by sodium chloride (this was not used with ceric salts, which would generate chlorine). The most effective tannings are those in which an oxidation plays a part (the metals pass from the higher to the lower valency) and those with alum, which cannot give salts of lower valency but are not very stable, and do not resist even the prolonged action of cold water (*pseudo-tanning*) Chromium salts are reduced to oxides by the skin and fixed, while oils and fats must be oxidised (to hydroxy-acids), as otherwise the tanning is not complete

R. Lepetit (*Ann. d. Soc. chim. di Milano*, 1907, p 83) asserts that in the tanning of sole and upper leather it is not sufficient to effect separation and stabilisation of the fibres, but that it is necessary to produce swelling and filling of the interstices between the fibres with *phlobaphenes*. These are colloidal substances dissolved or suspended in the tannin extracts and consisting partly of internal anhydrides of soluble tannins (*see* p 582) and partly of condensation products of formaldehyde with polyphenols and phenolcarboxylic acids derived from the tanning vegetable organisms. Indeed, according to Nierenstein, the products of the reaction between formalin and poly phenols exhibit tanning properties, and at the present time glove leather is successfully tanned by formaldehyde (Trillat and Payne). Also Weinschenck (1907–1908) stated that α- and β-naphthols in presence of formaldehyde are able to tan hides, but this is denied by Stiassny and Riccvuto (1908). In tanning with quinone derivatives (suggested by Meunier and Seyewetz) leather is formed, owing to the hydroquinone derived from the quinone reacting with the amino-groups of the proteins. With formaldehyde, there is probably production, by aldol condensation, of complex colloidal polymerides of formaldehyde (especially in presence of alkali carbonate), these reacting with amine complexes in the same way as formaldehyde and the aldols react with aniline (*see* p. 558). Thuan (1909) found that if the hides are previously treated with formaldehyde subsequent chrome tanning is hastened.

Mineral tanning is usually a rapid process, and the alum combines with the corium and preserves it, but the leather is not so lasting as that prepared with tannin and can still be gelatinised by prolonged boiling with water.

Chromium salts (the alum and chloride) are often used nowadays in place of alum and sodium chloride.

(2) **Chrome Tanning** has assumed considerable importance of recent years (since 1895), as it is rapid and furnishes boot leather highly resistant to wet; it is often used also for girths, &c. (*see later*, Rapid Tanning).

This method of tanning can be carried out in two baths or in a single bath. In the first case, the prepared hides are steeped in a cold bath containing 40 grms. of dichromate and 40 grms. of hydrochloric acid for every four litres of water and for every kilo of hide. Only one-half of the reagents are added to the bath at first, the hides being stirred with a reel for 2 to 3 hours, after which the remainder of the reagents is added and the stirring continued for 1 to 2 hours. The hides are then removed from the bath, allowed to drain, stretched, and placed in the reducing bath containing 105 grms. of sodium thiosulphate per 4 litres of tepid water and per kilo of hide. Here they are stirred for half an hour, after which 50 grms. of hydrochloric acid are gradually added (in the course of 1 to 2 hours) per kilo of hide; the hides are finally rinsed with water and the tanning is at an end. When, as is now more commonly the case, a single bath is used, this contains a solution of either basic chromium oxychloride, $Cr_2(OH)_5Cl$, and common salt, or *chromo-base*, which is a basic sulphate prepared by the firm of Lepetit, Dollfuss, and Gansser; the procedure is as in the preceding case. The use of chromium lactate has been recommended, since lactic acid reduces chromium salts, even in the cold.

(3) **Oil Tanning** or *chamoising*. This is used to obtain very soft leather for gloves, clothing, &c. Deer, stag, lamb, kid skins, &c., are smeared or rubbed with various fats (fish oil, wool fat, paraffin, egg-yolk, alum, carbolic acid, sodium chloride, &c.), the absorption of which is effected by repeated working of the skins, followed by drying in tepid chambers; the skins are thus rendered impermeable, while they can be washed many times without losing their tanning. The superficial fat is finally removed by washing in soda solution, the emulsion thus formed, known as *dégras* (*see* p. 389) being used for currying ordinary hides.

Heavier hides (cow, horse, ox, buffalo) intended for saddlery are subjected to mineral tanning (without being treated with lime) and afterwards to a kind of oil tanning which imparts to the leather considerable resistance to tension.

(4) **Ordinary Tanning** (*vegetable tanning*). The fresh hides as they come from the slaughterers are termed *green hides*, and in this condition an ox-hide will weigh from 30 to 40 kilos, its weight being reduced to one-half by tanning. Many hides are imported from South America in the dried and salted or smoked state. Ox-hides give the heaviest leather for boot-soles, while for lighter soles cow-hide is used; the uppers are made preferably from calf-skin. Saddles are made from horse-hide, pig-skin, and seal-skin, while sheep-skin is used for bookbinding leather and goat-skin for morocco leather. Deer-skin, goat-skin, &c., are tanned with oil to obtain chamois or buff leather (*see above*).

The hides are first *softened* by soaking for 2 days or longer (according as they are green or dry) in water, which removes blood and other adherent impurities. They are then placed on a "beam" (Fig. 411) and scraped on the flesh side with a curved knife (Fig. 412), which is drawn across them horizontally. They are then soaked for 24 hours, scraped again, washed in water for a few hours, thrown on the beam and allowed to drain. This operation is hastened if the softened hides are subjected to fulling in a revolving vessel (Fig. 413) or in a vat containing cold water in which they are worked with wooden mallets.

In order to remove the hair fixed in the epidermis (not in the corium), the epidermis must be attacked and almost destroyed, this being effected in various ways (by putrefaction, lime, or sulphides). Putrefaction ("sweating") is carried out by salting the flesh side of the hides or sprinkling them with crude acetic acid, bending the hides in two longitudinally with the hair outside and stacking them in tanks or in a warm chamber (30° to 50°); fermentation soon sets in, accompanied by heating and evolution of ammonia, the hides being then unhaired on the beam with a suitable knife. In order to avoid the possibility of excessive heating, the hides are sometimes placed in cement troughs fitted with perforated, wooden, false bottoms, water being sprayed on to the hides at the top, so that the temperature is kept down to 10° to 12°; after 8 to 12 days the hides can be

readily unhaired. The more delicate skins of small animals are treated with sulphides, being smeared with *rusma*, which consists of a mixture of 1 part of arsenic sulphide (orpiment) with 2 to 3 parts of slaked lime; calcium hydrosulphide is also used and gives better results. In recent years, sodium sulphide has also been used for heavy hides, unhairing being easily carried out by scraping the hides (after washing) with a knife against the set of the hair, the operation being facilitated, if necessary, by sprinkling a little sand or ashes on the hide; the hair serves for the manufacture of felt, but that treated with sulphide is converted into fertiliser. When unhaired, the hides are well washed in water and beaten on a large beam with the hair side uppermost; if necessary, the removal of the flesh is then completed by means of a knife, the useful part of the hide, *i.e.* the corium, then remaining.

The hides have by this time lost about 12 per cent. in weight, and those which have been limed are next kept for two or three days in several successive infusions of barley flour or bran ("bran drench") in active acid fermentation; to these are added sulphurous or sulphuric acid, lactic acid (or better, according to Boekringer, Ger. Pat. 234,584 of 1909, a solution of lactic anhydride in ammonium lactate), or acetic acid, the calcium soaps on the hides being thus decomposed; the acids separate at the surface and the soluble calcium salts

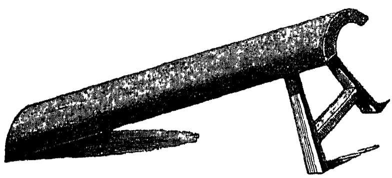


FIG. 411.

FIG. 412.

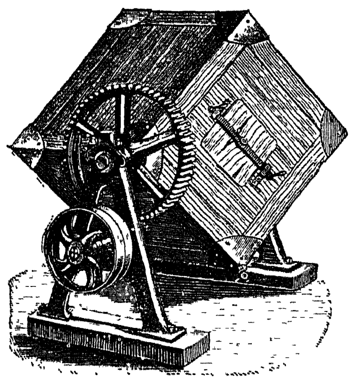


FIG. 413.

are eliminated by washing (at one time, mixtures of dog and bird dung with water were used, the action of these being due to enzymes and amine hydrochlorides). After a few days the hides swell up to double their original size and become yellowish and transparent. Excessive swelling is prevented by the addition of a little tanning material to the infusion.

All these preparatory operations are required to make the material to be tanned more permeable and more uniform in its behaviour towards the tanning agents, which are fixed to the extent of about 30 per cent. (calculated on the dry corium).[1] The tanning can now be carried out by the following methods:

(*a*) *Infusion tanning.* This process, which is used for lighter hides, consists in passing the hides into tanning baths of gradually increasing strength, so that the tanning may be gradual and penetrative. The total time required is 6 to 9 weeks, and between each bath and the succeeding one the hides are drained, pressed, and fulled in order to facilitate the absorption of the tannin.

(*b*) *Tanning in layers* was once largely used but is now employed more particularly for sole leather. Fifty or sixty hides are placed, alternately with layers of powdered or crushed tanning material (bark, wood, &c.), in a cement or wooden vessel, the empty spaces being then filled with the tanning material and the whole covered with water. The vessel is then closed with an air-tight cover and left for about 2 months, the hides being then transferred to a second similar vessel containing rather less tanning material, where they are left for 3 to 4 months, and finally to a third vessel containing still less tanning material (4 to 5 months).

[1] F. Carini (*Ann. d. Soc. chim. di Milano*, 1903, p. 23, and 1904, p. 144) proposes to use the hydrostatic balance in order to obtain the weight of the dry hide from that of the wet hide, without drying. The hides can thus be followed through all the operations, from their entry in a more or less moist state. The quantity of tanning material fixed can also be determined at any moment in this way.

If the hides are very heavy and resistant, they are passed to a fourth and sometimes to a fifth bath or pit, the whole operation then occupying about two years and the consumption of bark being about five times the weight of the dry hides. The completion of the tanning is ascertained by cutting the hide and observing that the section is uniform and without horny or fleshy layers, and that the grain does not crack when the hide is carefully bent.

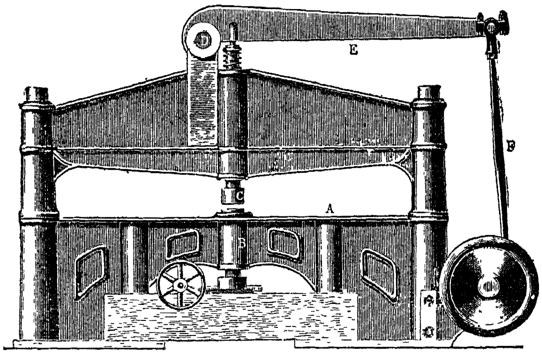


FIG 414.

(c) *Rapid tanning*, which gives a greater output of leather, has been attempted in many different ways: By immersing and compressing the hides in relatively concentrated tanning baths prepared from active, modern extracts, and containing a certain amount of acid to prevent wrinkling of the hides, the tanning liquor being circulated by means of pumps without moving the hides; or the skins are placed in revolving barrels or drums, the lower half dipping into tanning liquor so that the hides are pressed at intervals. The diffusion process is also applied by placing the tanning bath in bags composed of various hides sewn together. Tanning in a vacuum has likewise been used in order to effect better penetration of the tanning material, considerable pressure being exerted automatically on the hides at regular intervals, and the operation being facilitated by gentle heat, &c. By these rapid processes (*see also* Use of Quinone, Ger. Pat. 206957, 1907) tanning can be completed in 6 to 8 weeks, this including the preliminary preparation of the hides. The actual tanning may, indeed, be limited to 30 hours if revolving barrels are used with hot, highly concentrated tanning baths (8° to 10° Bé). When such a rapid process is used it is, however, indispensable to eliminate all traces of lime beforehand by immersion in formic acid solution. Other very rapid methods which are largely used are chrome tanning (*see above*) and formaldehyde tanning as proposed by Payne.

The tanned hides are then subjected to *finishing*, which varies considerably with the nature of the hide and the kind of leather required.

For sole leather, the hides from the layers are first dried in the shade and are then beaten or hammered by means of a suitable machine (Fig. 414); in this way the leather is rendered more compact, so that the wear of the sole is diminished. To make the leather of uniform thickness and to eliminate lumps, scurf, wrinkles, &c., the hide is scraped or shaved on the under side (*i.e.* not the hair side) with a sharp curved knife or, better, with a machine carrying steel blades on a moving band, which can be brought more or less near to the skin, the latter being stretched on a movable trolley (Fig. 415) so as to facilitate this tedious and troublesome operation. Regular *graining* is attained by stretching the hide on a bench, one side being fixed to the edge of the bench and the hide then bent over on itself, while a block of wood having a concave base with pointed grooves (Fig. 416) is moved backwards and forwards over the fold, which is gradually displaced until the whole surface of the hide is covered.

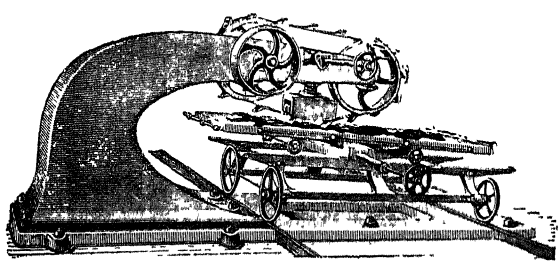


FIG. 415.

Artificial grain is nowadays imparted by pressing the hides between special fluted cylinders.

Those hides which are required to show, not graining, but a smooth surface are first rendered perfectly uniform at the surface by rubbing both sides with pumice by hand or

more conveniently by a kind of spindle-shaped grindstone covered with emery (Fig. 417), against which the surface of the hide is gently pressed. In some cases this operation is completed by polishing the bloom side with a concave piece of wood, similar to that of Fig. 416, but with a smooth surface lined with cork.

The polishing is finished on the bloom side with a heavy, very smooth roller, moved horizontally by a rod connected with an eccentric. All these finishing operations are carried out mechanically by machines which are continually being improved and which cannot be described here.

Finally, many leathers with which a certain degree of softness is required, are greased with fish oil or a mixture of this with tallow or other fats (wool fat) or dégras (*see* p. 389). In this operation, which amounts to a second tanning (chamoising, *see above*), the tanned and still moist hides are well smeared with the fat and exposed to the air until the whole of it is absorbed.

Leather for boot uppers is coloured black on the flesh side by rubbing with concentrated solutions of iron acetate and sulphate, treating with oil, wax, soap, lampblack, &c., and then polishing with smooth wood until a shining surface is obtained.

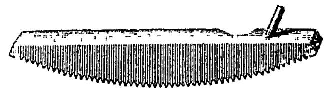


FIG. 416.

For special purposes hides and leathers are coloured with basic or mordant aniline colours, the hides being first prepared by immersion for 12 hours in cold water in which is dissolved the white of an egg for each hide. The dyeing is carried out at a temperature of 30°. Certain leathers are varnished with ordinary resin varnishes. In order to supply the great demand for large hides for the hoods, &c., of carriages, ox-hides and cow-hides are nowadays divided, the more resistant part being kept for the hoods, and the flesh side for the seats, &c.

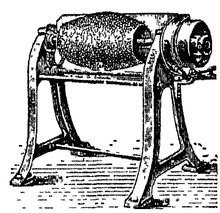


FIG. 417

The use of pure water is indispensable in all tanning operations, since water which is too hard and rich in lime readily produces white efflorescence on the hides. The presence of iron in the water results in the formation of dark patches, while suspended organic matter is always harmful; waters containing these substances must hence be thoroughly purified before use (*see* vol. i, pp. 218 and 665). In order to avoid the formation of the white efflorescence—due to the combination of lime with the fatty matters of the tanning materials—it has been proposed to replace the fats by mineral oils, which do not give calcium salts, or to wash the hides well with dilute lactic or formic acid which form soluble calcium salts. The suggestion has also been made that the hides be dressed, not with fats, but with the anhydrides or lactones of fatty acids, as these form calcium salts more slowly (the *purgatol* recently placed on the market consists mainly of anhydrides or lactones).

England's exports and imports of hides are as follow:

		Imports	Exports
Raw hides	1910	£12,882,326	£1,757,762
	1911	11,104,326	1,685,583
Tanned hides, leather	1910	11,824,741	4,686,485
	1911	12,227,606	4,880,932

O. HYDROGENATED BENZENE COMPOUNDS

Considerable interest attaches to the numerous *hydrophthalic acids* studied by Baeyer in their various constitutional and stereo-isomerides (*cis-* and *trans-*isomerides; *see* p. 21).

They behave largely like unsaturated aliphatic compounds (*see* p. 520), as they no longer possess the stability of the true benzene nucleus. The position of the true double linkings in these compounds is determined by the addition of bromine or by subsequent elimination of the latter by reduction, with or without substitution of hydrogen, according as the two bromine atoms are in para- or ortho-positions. Simple boiling with alkali often effects displacement

of a double bond (as with oleic acid; *see* p. 293), so that it is possible to pass from one isomeride to another.

The di-, tetra-, and hexa-hydrophthalic and terephthalic acids can be dehydrogenated in stages by heating with bromine at 200°; many of them form anhydrides.

From the results of his investigations on the hydrophthalic acids Baeyer drew important conclusions concerning the constitution of the benzene nucleus.

Many important hydrogenated benzene derivatives occur naturally, among them the *naphthenes*, found in abundance in Russian petroleum (*see* p. 63), which contain hexamethylene groupings (*see* Polymethylenes, p. 520) Synthetically they may be obtained, for example, from calcium pimelate:

$$CH_2{<}{\substack{CH_2\cdot CH_2\cdot CO_2 \\ CH_2\cdot CH_2\cdot CO_2}}{>}Ca = CaCO_3 + CH_2{<}{\substack{CH_2\cdot CH_2 \\ CH_2\cdot CH_2}}{>}CO \text{ (\textit{ketohexamethylene})}.$$

Also, by condensing 2 mols. of ethyl succinate with sodium and then hydrolysing the product and heating at 200°, *p-diketohexamethylene* is obtained. Hydrogenation of benzene and its homologues, by passing their vapours, mixed with hydrogen, over heated finely divided nickel, yields *hexamethylene* [1] and its homologues, *hexahydrophenol* (b pt. 160·5°), and *p-diketohexamethylene* (m.pt. 78°). The latter gives the corresponding alcohol, *quinitol* (*p-dihydroxyhexamethylene*), which forms various *cis-* and *trans-*isomerides. *Inositol*, $C_6H_{12}O_6$, the hexahydric alcohol derived from hexamethylene, is isomeric with the hexoses, but with HI or PCl_5 yields true benzene derivatives.

Various *naphthenic acids* are obtained by oxidation of the naphthenes of petroleum (*see* p. 63), and are distinguished from open-chain acids by forming soluble magnesium and calcium salts; by this means they can be detected when used in the manufacture of soaps.

Still more interesting are the *terpenes* and the *camphors*, which are found in various plants and form the principal constituents of many *ethereal oils* and *essences* and of many *resins*.

QUINIC ACID (Tetrahydroxyhexahydrobenzoic Acid), $CO_2H\cdot C_6H_7(OH)_4$, is optically active, but only an inactive modification is known. It is obtained from the roots of coffee, cinchona, &c., and forms white crystals.

TERPENES

These are regarded chemically as hydrogenated derivatives of cymene (dihydrocymene) and its homologues, and have the generic formula $C_{10}H_{16}$. They are not soluble in water, but can be readily isolated from the natural products owing to their volatility in steam.

The chemical constitutions of the principal terpenes have been established mainly by O. Wallach's investigations over a period of more than twenty years. By their syntheses, their halogenated additive compounds, their behaviour towards oxidising agents and their molecular refraction (*see* p. 26), it has been shown that they contain two double linkings and a closed ring of six carbon atoms.

There is, however, a group of more complex terpenes (pinene, camphene, fenchene, &c.) which have only one double bond. In order to define the position of the double linkages (Δ), Baeyer numbered the fundamental carbon atoms of the cymene as in the first figure of the following scheme, which shows the

[1] **HEXAMETHYLENE** (*hexahydrobenzene*, *cyclohexane*, or *naphthene*) is found in Caucasian petroleums and is obtained synthetically from iodohexamethylene or 1 : 3-dibromopropane. It is a colourless liquid smelling like petroleum, and it boils at 80° and resists the action of permanganate. By hydriodic acid at high temperatures it is converted into methylpentamethylene.

constitution of five *terpadienes* out of fourteen possible theoretically without counting enantiomorphs.

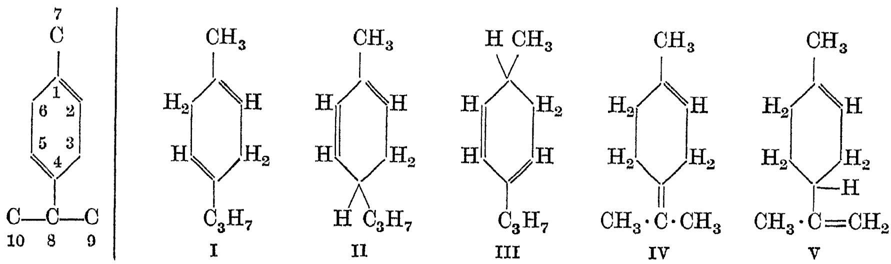


FIG. 418.

To indicate the position of the double linking in the side-chain, instead of giving only the lower number of the two carbon atoms united to the double linking, as in the case of the nucleus (*e.g.* III = $\Delta^{3,5}$-terpadiene or *limonene ;* I = $\Delta^{1,4}$-terpadiene), the numbers of both the carbon atoms united to the double linking are given, the higher number being bracketed (*e.g.* IV = $\Delta^{1,4(8)}$-terpadiene ; V = $\Delta^{1,8(9)}$-terpadiene). In the official nomenclature the name *terpane* is given to **Hexahydrocymene**, $C_{10}H_{20}$. **Tetrahydrocymene**, $C_{10}H_{18}$, being called *terpene* and the **Dihydrocymenes**, $C_{10}H_{16}$, *terpadienes.*

As separated from plants or fruits, the terpenes are generally mixtures, and when obtained from conifers are termed *oil of turpentine.* Essence of lemon gives *citrene ;* thyme, *thymene ;* cumin, *carvene ;* orange, *hesperidine,* &c. Although their boiling-points differ little (160° to 180°), they form tetra-bromo-derivatives and dihydrochlorides with widely different melting-points, these compounds hence serving for their separation.

Properties. Owing to the presence of double linkings, which act as in aliphatic compounds, the terpenes can combine with four bromine atoms or two mols. of HCl (the halogen being readily replaced by hydroxyl, with formation of camphor) and also react with nitrous acid or nitrosyl chloride, forming solid **Nitrosites**, $C_{10}H_{16}(NO_2)(NO)$, or **Nitrosochlorides**, $C_{10}H_{16}(NO)Cl$, which are also solid and sometimes blue.

They oxidise easily and with mild oxidising agents give benzene derivatives, whilst on energetic oxidation they resinify ; they polymerise readily, and by acids, for instance, are converted into more stable isomerides. In alcoholic solution they give characteristic colorations with concentrated sulphuric acid. They are usually optically active.

They often accompany the *natural perfumes* of fruits and flowers, which, now that they have been subjected to thorough chemical study, can be obtained purer and of increased value.[1]

[1] **PERFUME INDUSTRY.** A considerable number of the *natural perfumes* have been prepared from the very earliest times, but with the perfected methods of extraction now available they are obtained in higher yields and in a more highly refined condition. The most abundant supplies of raw material have always been, and are still, obtained from eastern countries, where whole provinces are often devoted to the cultivation of flowers.

The most delicate perfumes are those obtained from flowers which contain, along with the odorous principle, other substances which refine the aroma and render it softer. The name artificial perfumes was at one time given to mixtures, in proportions carefully chosen, of the fundamental natural essences, a great variety of perfumes being thus obtained ; this, however, required a very highly developed sense of smell in the operator.

The discovery of artificial perfumes did not diminish the consumption of the natural products since these became cheaper and thus appealed to a large public.

The consumption of perfumes fluctuates with the fortunes of a nation. The early Eastern races and then the ancient Egyptians introduced perfumes into religious ceremonies, their secular use being often forbidden. Gradually, however, they became used for domestic purposes, together with many different pomades and, in some cases, dyes. Egyptian pomades were held in high esteem by Cleopatra. With the ancient Greeks, the use of perfumes and cosmetics assumed considerable importance and often degenerated into abuse, and Socrates states that if even a slave is anointed with a good perfume he will exhale the same odour as his master.

Perfumery flourished under the Romans and declined with the Empire, being re-established in Italy only a

CINENE (**$\Delta^{1,8(9)}$-Terpadiene or Dipentene; Inactive Limonene**), $C_{10}H_{16}$, is found together with cineol in *oleum cinæ* and also in *Laurus camphora* and in Russian and Swedish turpentine oils. It is formed by isomeric change when camphene, active limonene, pinene, &c., are subjected to protracted heating at 260° to 270°, and is obtained, together with isoprene, when rubber is distilled, 2 mols of the *isoprene*, $CH_2 : CH \cdot C(CH_3) : CH_2$, undergoing condensation.

It has a pleasant odour of lemons, and boils at 176°. **Nitrosodipentene** (inactive

the time of the Renaissance It then passed into France, where it became a true national industry, culminating at the time of the perfumed Court of Louis XV.

Until about the middle of last century, France enjoyed almost a monopoly in this industry, but when science pervaded this branch of human activity, the clever French rule-of-thumb manufacturers did not grasp quickly enough the benefit to be derived from a rational development of their industry, of which England and Russia, and more especially, during the past quarter of a century, Germany have taken advantage. At Grasse and Cannes, in the south of France, however, the natural perfume industry is still of importance, certain factories dealing with as much as 3000 kilos of violets (40 to 50 millions of flowers) at a time.

As has been already mentioned, the prime materials come mainly from Eastern Europe, and at the present time also from the Far East. But the cultivation of plants for perfumes is still largely carried on in the South of France and in Sicily

In annuals the essential oil is formed in the green organs, and the majority of it is found in the flowers before ertilisation The extraction of perfumes from flowers and leaves is carried out in various ways : (1) By *distillation* with direct or indirect steam or *in vacuo*, the distillates of different densities being separated ; this method is used for *lavender*, *rosemary*, *thyme*, *orange blossom*, and *roses*, which are unaltered at steam heat. (2) By *infusion* for 12 to 48 hours at 60° to 65° with pure fats (olive oil, &c.), the flowers being renewed four to six times until the fat is highly perfumed , the extracted flowers are pressed to free them from fat, and the perfumed fat run into enamelled iron vessels as a concentrated pomade , in this way are treated *cassia*, *violets*, *jonquils*, and sometimes orange blossom and roses, when mixed with other flowers. (3) By *absorption in the cold* of the more delicate perfumes of *jessamine*, *heliotrope*, and *tuberoses ;* in vessels with glass walls smeared with fat or covered with cloth soaked in oil, the petals are pressed and rubbed, being renewed every day ; after some days or at the end of the season the perfumed fats are shaken for a long time with alcohol, which extracts all the perfume. To obtain colourless products, Piver passes a slow current of air through the flowers and then on to the fatty surface. (4) By *dissolution* The use of this method is spreading, as it gives highly concentrated, very delicate perfumes. The flowers are immersed in petroleum ether, carbon disulphide, &c., the perfume being extracted by a current of steam from the solvent, which is afterwards recovered. (5) By *pressure* with hand or hydraulic presses, this method being employed with orange-peel, bergamot, iris rhizomes, &c. The yields obtained per 1000 kilos of leaves or flowers are about as follow : 1 kilo of *orange oil* or *neroli*, from the flowers (value £24 to £28), or 3 kilos of *petit grain* (from the leaves) ; 1 kilo of *essence of basil* (£6 to £8 per kilo) ; 1200 grms. of *essence of citronella* (88*s*. per kilo) ; 9 to 15 kilos of *eucalyptus oil* (from the leaves) ; 120 grms. of *essence of jessamine* (from fresh flowers) ; 1 kilo of *geranium oil* (from flowers and leaves) ; 10 kilos of *oil of lavender ;* 6 kilos of *marjoram oil ;* 2 kilos of *mint oil ;* 3 kilos of myrtle oil ; 2 to 10 kilos of *rosemary oil* , and 200 to 500 grms. of *rose oil.*

The exports from Sicily and Calabria and the imports to Italy of essences were as follow :

Exports from Sicily and Calabria		1906	1907	1908	1909	1910
Orange oil . .	kilos	136,739	162,274	173,265	242,762	143,825 (£97,800)
Bergamot oil . .	,,	63,510	87,538	74,842	73,803	61,788 (£82,930)
Lemon oil . .	,,	440,500	469,385	476,842	361,647	425,076 (£154,025)
Various (mint, mandarin, &c) oils . . .	kilos	—	—	28,500	31,800	13,500 (£14,800)
Imports into Italy						
Clove oil	kilos	2,446	2,165	1,538	1,969	1,878 (£1,502)
Mint oil	,,	6,628	6,484	4,391	5,334	8,931 (£14,290)
Rose oil . . .	,,	493	341	101	158	109 (£3,920)
Various oils . .	,,	67,797	77,510	81,830	90,661	99,228 (£79,380)

As much as 100 quintals of flowers for perfumes (at 28*s*. per quintal) are dispatched per day from San Remo n the spring and summer.

In the neighbourhood of Grasse, Cannes, and Nice the production in 1902 was 2,500,000 kilos of *orange blossom*, 3,000,000 kilos of *rose leaves*, 200,000 kilos of *jessamine*, 150,000 kilos of *violets*, 150,000 kilos of *tuberoses*, &c., all these being extracted on the spot.

In Germany, although the climate does not seem very favourable, the cultivation of certain flowers for perfumes is largely carried on in some districts. The perfumery factories have hundreds of hectares of land under flowers not only for commercial purposes, but also for analytical and research work One hectare yields 10,000 to 15,000 kilos of rose leaves. At one time the firm of Schimmel (Leipzig) treated as much as 600,000 kilos of fresh rose leaves per day, 300 kilos of *rose oil* being extracted ; this was repeated two or three times in a month (June). A kilo of the oil is sometimes obtained from 2000 kilos of the leaves.

Rose cultivation is, however, carried on most extensively in Turkey and Bulgaria, where preference is given to the red rose (*Rosa damascæna*), which gives on an average 1 kilo of oil per 4000 kilos of leaves, although white roses (*Rosa alba*), giving 1 kilo of oil per 5000 kilos of fresh petals, are also largely grown. The product from the latter variety is less fine, but it gives an oil crystallising at 18° to 20° and is used to mask oils of lower quality ; the market value of the oil is judged more particularly from the freezing-point, which should be between 17° and 19° for good qualities. Adulteration with alcohol or spermaceti is easily discovered, but it is more difficult to detect additions of geranium oil or palmarosa oil.

In 1887 Turkey produced 2400 kilos of pure rose oil (attar of roses), whilst in 1904 and 1906 the output reached 3600 kilos. The annual production varies very considerably, as the plants suffer greatly in dry seasons, especially water is scarce in the month of May preceding the harvest; in 1907 indeed, the output was only 2000 kilos.

carvoxime) melts at 93°. With HCl, cinene gives two stereoisomeric *dipentene dihydrochlorides* (1 : 4-dichloroterpanes), melting at 50° and 25°. The *tetrabromide* melts at 125°.

CARVENE (*d*-Limonene, Hesperidine, Citrene), $C_{10}H_{16}$, forms the greater part of orange-peel oil and also occurs abundantly in cumin oil, anethum oil, &c. ; lemon oil is a mixture of pinene and limonene. It is a liquid boiling at 175° and is optically active although readily convertible into inactive dipentene. It forms a dextro-rotatory tetrabromide melting at 104°.

In Bulgaria roses are still more largely grown, and here, too, the production varies widely. The exports of pure oil were as follows: 3190 kilos (£71,280) in 1897, 3900 kilos in 1902; 6200 in 1903; 5000 in 1904; less than 4500 in 1905. In 1907 the exports were valued at £168,000, and in 1908 at £184,000; in 1909 6053 kilos were exported. At one time two-thirds of the oil went to France, but now only one-third goes to the French factories the rest being sent to England and Germany.

In 1910 England imported natural ethereal oils to the value of £320,218, artificial ethereal oils to the value of £34,369, and alcoholic perfumes to the value of £90,176. The United States imported perfumes and other toilet preparations to the value of £303,600 in 1911.

The price of *attar of roses* varies from £32 to £80 per kilo, and was formerly higher than this.

In 1901 H von Soden patented a process for obtaining more refined and delicate perfumes from flowers. He first obtained a petroleum ether extract which was then evaporated and the residue taken up in alcohol, the latter being distilled off and the residue distilled in steam. It must, however, be pointed out that with this process, 1 kilo of the finest rose oil would now cost £1520 and 1 kilo of oil of violets almost £4000.

From what has been already stated, it will be recognised that considerable interest attaches to the study of the composition and constitution of these essences and to their artificial production by synthetical methods. In former times, various artificial perfumes have been obtained empirically, as was also the case with the first coal-tar dye, yet it has required systematic chemical investigation to open up new fields in this direction During the last thirty years, the consumption of perfumes has increased from £480,000 to £2,400,000, owing to the diminished prices of the natural and artificial products.

The first artificial perfume was nitrobenzene or artificial myrbane oil, which was discovered by Mitscherlich in 1834, placed on the market by Colles and manufactured on a large scale by nitrating benzene from tar by Mansfield in 1847 In about 1840, Piria oxidised *salicin* (a glucoside found in willow bark) and thus obtained salicylaldehyde, which is the pleasant smelling essence of *Spiræa ulmaria* (meadow-sweet). A few years later—in 1844—Cahours succeeded in isolating the active principle of *gaultheria* or *wintergreen oil*, consisting of methyl salicylate, which can be obtained synthetically by heating salicylic acid with methyl alcohol (wood spirit) and sulphuric acid. Many of the natural perfumes contain aldehydes, and in 1853 Bertagnini showed how they could be separated pure by first combining them with bisulphite. *Benzaldehyde* was synthesised by Cahours in 1868, and *coumarin*, the essence of *Asperula odorata* by Perkin in 1875 In 1876 Haarmann and Tiemann ascertained the constitution of *vanillin*, later preparing it from coniferin or, better still, from eugenol extracted from clove oil. In 1888 Baur prepared *artificial musk*

In 1893 Tiemann and Kruger succeeded in effecting the synthesis of violet oil, previously obtained at enormous expense from the natural flowers and costing more than £600 per kilo. They also separated *irone*, the odorous principle of iris root, and determined its chemical constitution. Immediately afterwards they prepared synthetically an isomeride of irone, *ionone* (*see later*) to which the delicate odour of the violet is due. These investigators heated citral, which occurs in abundance in lemons, with acetone, acetic anhydride, acetic acid, and sodium acetate, obtaining first pseudo-ionone, which has an unpleasant smell, and, when treated with mineral acid, yields ionone. These processes were patented by Tiemann and disposed of by him to the most important perfume manufacturers for £10,000.

The study of the chemical constitution of the components of perfumes reveals a certain relation between the aroma and the presence of definite atomic groupings (*osmophores*) and attempts were made to establish a perfume theory on a similar basis to the colour theory of aniline dyes, the characteristic groups of which are termed *chromophores*. It has not yet been found possible to formulate a theory as rigorous as that for the colouring-matters, and all that has been fixed is that aldehydes, ketones, mixed ethers, &c., often enter into the constitution of perfumes, and that the introduction of certain alcoholic residues into the molecules may intensify or modify the aroma.

The action of perfumes on the olfactory nerves is not thoroughly understood, although it is regarded by some as due to vibrations of the ether similar to those by which light and heat are transmitted, these vibrations originating from the oxidation of the substance in the air. This hypothesis seems to be supported by the fact that many odorous substances emit no smell when worked and distilled in an inert gas instead of in air. It is now, however, generally assumed that the smell is propagated by small particles or molecules, which become detached and, in the state of gas, come into contact with and excite the papillæ of the nasal mucous membrane. The fact that certain substances have little smell in the pure or concentrated state and acquire their maximum smell only when considerably diluted, is well explained by modern views on solutions, dissociation in dilute solutions giving rise to the corresponding ions, which become detached and excite the olfactory sense. That minimal traces of these substances transmit perfume is shown by the retention of this property by garments which have been washed five or six times *see* Experiment described in vol. i, p. 3). A series of tests, controlled by the *olfactometer*, showed that most men—who have by no means a very delicate sense of smell in comparison with other animals—perceived the odour of 1 part of prussic acid in 100,000 of water, 7 per cent. of the individuals examined detecting it in a dilution of 1 in 2,000,000. Of the women tested, however, not one was able to detect prussic acid in a dilution as small as 1 in 20,000. These results support the view that male animals are very sensitive to the odour of the females, which serves to excite their sexual passions. Some individuals, termed *anosmic*, are quite without sense of smell.

The following data give an idea of the influence exercised by the artificial products on the prices of perfumes in general: vanillin cost £120 per kilo in 1878, £35 in 1890, and £3 in 1892, while for heliotropine the price was £100 per kilo in 1881, £15 in 1890, and about 30*s*. in 1902. That the consumption of the natural products has not been diminished but has increased is shown by the importation of vanilla to France, which amounted to 29,000 kilos in the period 1857–1866, and to 137,000 kilos in 1887–1896.

For the year 1897 it was calculated that the total imports into and exports from Germany of ethereal oils and perfumes amounted to £920,000.

The Italian imports of alcoholic perfumes in 1904 were valued at £18,640 and those of non-alcoholic at £18,560, while the exports were valued at £3440 and £16,000 respectively.

For fruit essences *see* p. 371.

l-LIMONENE, $C_{10}H_{16}$, the constitution of which is shown on p. 593 (V), can be obtained from d-carvone, and occurs, together with l-pinene, in pine oil. Its tetrabromide melts at 104°.

SYLVESTRENE, $C_{10}H_{16}$, is possibly derived from m-cymene and forms a dextro-rotatory component of turpentine. It boils at 176° and gives an intense blue coloration with concentrated sulphuric acid and acetic anhydride.

TERPINOLENE ($\Delta^{1,4(8)}$-Terpadiene), $C_{10}H_{16}$, has the constitution shown at IV on p. 593. It is obtained by the elimination of water from terpineol and melts at 185°.

TERPINENE, $C_{10}H_{16}$, boiling at 179° to 180°, is obtained in the transformation of various terpenes. Its nitrosite forms monoclinic crystals melting at 155°.

DIHYDROCYMENE, $C_{10}H_{16}$, obtained synthetically from ethyl succinylsuccinate, boils at 174°.

PHELLANDRENE, $C_{10}H_{16}$, is known in both the lævo- and dextro-rotatory forms, these having the same chemical and physical properties (excepting the optical rotation) and boiling at 172°. The former (l-) is found in Australian eucalyptus oil and the latter in *Anethum fœniculum* and in water-fennel oil (*Phellandrium aquaticum*).

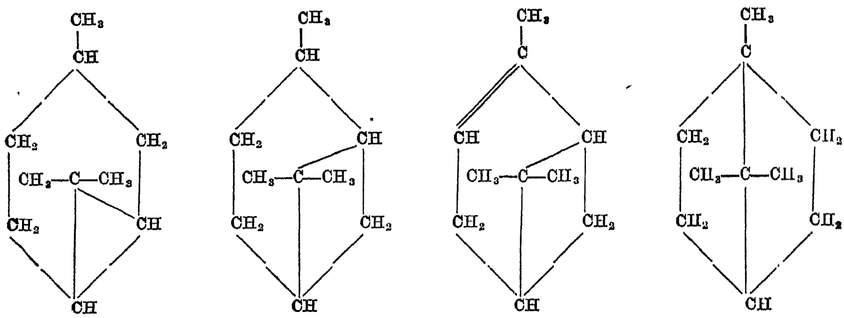
MENTHENE, $C_{10}H_{18}$, boils at 167°. MENTHANE (Hexahydrocymene), $C_{10}H_{20}$, boiling at 170°, does not occur naturally, but is obtained by hydrogenating cymene in presence of nickel.

COMPLEX TERPENES

Like the preceding, these are composed of a monocyclic system, but with two rings; they have only one double linking, and hence combine with two atoms of hydrogen or halogen.

They can be converted readily into cymene and its derivatives.

The following four diagrams show how a trimethylene ring or *bridge* is formed in **Carane** (not known in the free state, although the corresponding saturated, synthetic ketone, **Carone**, is known), a tetramethylene ring in pinane and pinene, and a pentamethylene ring in camphane :



Carane Pinane Pinene Camphane

PINENE (Terebenthene, Laurene, Menthene, &c.), $C_{10}H_{16}$ (constitution, *see above*), forms one of the principal components of oil of turpentine, occurs also in sage and juniper oil, and, mixed with sylvestrene and dipentene, forms Russian and Swedish turpentine oil.

When incisions are made at suitable seasons in certain varieties of pine, fir, and larch, a kind of balsam is exuded in the form of a juice which gradually changes to a soft resin, more or less clear according to the quality. This is known as *ordinary turpentine* or American, French, Venetian, according to the particular tree and to the locality of origin. When turpentine is distilled with steam, the liquid *essence* or *oil of turpentine* (turps) is collected separately, the residue, which is solid in the cold, being **Colophony**.[1] The direct extraction

[1] COLOPHONY (*rosin*) is hard and brittle, its sp. gr. being 1·050 to 1·085 at 15° and its fracture shining and conchoidal. According to the quality, its colour varies from yellow to brown, but it gives a whitish powder. At 70° it becomes soft and it forms a kind of emulsion with hot water. It always melts below 135° and it is readily soluble in alcohol (1 in 10), ether, benzene, petroleum ether, and carbon disulphide. It burns with a smoky flame and, when subjected to dry distillation out of contact with the air, yields *resin oil*. It contains *abietic acid*, $C_{19}H_{28}O_2$, which has two double linkings, melts at 165°, and is soluble in hot alcohol. From *gallipot rosin* (*Pinus maritima*) *pimaric acid*, $C_{20}H_{30}O_2$, m.pt. 148°, has been obtained.

Colophony has the rotatory power −69·6°, and the acid number 145 to 185.

One cubic metre of fir contains about 10 kilos of turpentine, which yields as much as 7 kilos of colophony,

of the turpentine from resinous woods by means of suitable solvents (hot wood-tar mixed with pine oil; U.S. Pat. 852,236) has been suggested. Oil of turpentine is rectified by heating with steam in presence of 0·5 per cent. of quicklime. As the oil always resinifies to some extent when exposed to the air, it is often desirable to redistil it before use. The strong and less agreeable odour of Russian and Greek turpentine oils is removed or lessened by shaking with a solution of permanganate, dichromate, or persulphate.

Fresh oil of turpentine is clear, colourless, and highly mobile; it has the sp. gr. 0·855 to 0·876 and boils at 156° to 161°. It absorbs and combines with considerable quantities of ozone and oxygen—part of the latter being converted into ozone and the oil at the same time resinifying. It dissolves sulphur, phosphorus, rubber, and resins, and is hence used for varnishes, lacs, oil paints, &c.[1]

Permanganate in acid solution transforms it partly into **Pinonic Acid**, $C_{10}H_{16}O_3$, while with dilute nitric acid it gives **Terephthalic** and **Terebinic Acids**, $C_7H_{10}O_4$. It reacts violently with iodine in the hot, forming cymene. The relation between resins and aromatic compounds is established by the fact that when the former are distilled with zinc dust they form aromatic hydrocarbons, while if fused with potash they give di- and tri-hydroxy-benzenes. Resin substitutes or *artificial resins* are now prepared by heating phenols with formaldehyde in presence of hydroxy-acids (*e.g.* tartaric acid) or mineral acids (Blumer, Eng. Pat. 12,880 of 1902, and Fr. Pat. 361,539 of 1905; also Baekeland, 1909).

According to the preponderance of lævo- or dextro-pinene, turpentine oil is lævo-rotatory (Venetian, German, and French) or dextro-rotatory (Australian).

Pinene contains only one double linking, and hence unites with only 1 mol. of HCl, giving **Pinene Hydrochloride**, $C_{10}H_{17}Cl$, which melts at 125°, and has the smell of camphor (**Artificial Camphor**). When treated with alcoholic potash, this hydrochloride is converted into **CAMPHENE**, $C_{10}H_{16}$, m.pt. 50°, which is known in three optical modifications and is

while 1 cu metre of pine gives 22 kilos of turpentine, this leaving 16·6 kilos of colophony; the larch gives an intermediate yield.

Colophony is used in large quantities for mixing with soaps (*see* Resin Soaps, p. 420), for sizing paper, for making varnishes, mastics, &c. In the United States 35 per cent of the total output is used in soap-making.

Large quantities of it are incorporated with artificial wax (cerasin), which is thus cheapened; to *deodorise* the resin, it is finely ground, macerated with dilute sulphuric acid for five or six days and then suspended in hot water and subjected to a jet of steam for some time. After this treatment it melts and mixes well with the cerasin.

Colophony is also used for making sealing-wax by mixing with shellac, turpentine, and a larger or smaller number of mineral substances (chalk, burnt gypsum, magnesia, zinc oxide, baryta, kaolin, &c.), according to the quality required; the fused mass is coloured with cinnabar (for the finer red qualities), minium, ferric oxide, or red ochre. The best qualities contain only 40 per cent. of mineral matter and are mainly shellac, while the inferior kinds contain as much as 70 per cent. of mineral matter, the residue being principally colophony. Sealing-wax is coloured black by lampblack or boneblack, green by Prussian blue, yellow by chrome yellow, or blue by ultramarine; when fused, colophony may be coloured also with algol or indanthrene dyes (*q.v.*).

Italy imported 18 quintals of sealing-wax in 1898 and 61 in 1910, the corresponding exports amounting to 21 and 86 quintals respectively.

In 1905 Germany imported 41,042 quintals of shellac and sealing-wax, of the value of £779,800, and exported 9575 quintals (£196,280).

In 1909 200,000 cases of sealing-wax were dispatched from Calcutta to England, Germany, and the United States.

The importation of colophony into Italy amounted in 1896–1899 to an average of 122,700 quintals; in 1905 to 125,000 quintals (£72,450); and in 1910 to 149,000 quintals (£119,200), mainly from North America. Its price varies from 12*s*. to 28*s*. per quintal.

In 1910 England imported 75,000 tons of rosin (colophony), of the value of £880,582, and 8700 tons of shellac and sealing-wax, of the value of £627,029. The United States exported 2,269,000 barrels (£2,474,800) of rosin in 1910 and 2,415,000 barrels (£3,241,600) in 1911, and imported 12,000 tons (£638,200) of sealing-wax in 1910 and 8000 tons (£478,600) in 1911.

[1] **OIL OF TURPENTINE.** Most common are the French, English, Russian, German, and American varieties, 40,000 tons of the last-named being landed at Hamburg, London, and Antwerp in 1897. In 1908 the output in the United States was 1,700,000 quintals (£2,800,000), one-half of this being produced in Florida.

In 1902 Germany imported 63,600 barrels, in 1906 about 68,000 barrels, and in 1908 77,000 barrels (68,000 from America and 9000 from France): in 1909 the imports were 318,884 quintals (£1,200,000), and the exports 12,457 quintals, 100,000 tons of turpentine resins and balsams (£880,000) being also imported, and 21,000 tons exported. In 1909 England imported 222,000 quintals of oil of turpentine, and in 1910 23,612 tons (£1,001,216), whilst the United States exported 14,252,000 gallons (£1,925,400) in 1910 and 18,198,000 gallons (£2,187,400) in 1911.

Italy's imports of oil of turpentine were as follow: 30,963 quintals in 1906; 30,088 in 1907; 33,316 in 1908; 26,932 in 1909, and 27,941 (£111,760) in 1910. In the United States (on the Savannah market) the output was calculated at 675,000 barrels in 1907–1908, 725,000 in 1908–1909, and 580,000 in 1909–1910.

In 1904 there were 1287 turpentine distilleries in the United States, with a total capital of £1,400,000, and in 1909 1585 distilleries with a capital of £2,480,000 and an output valued at £5,200,000.

The price varies from 56*s*. to 76*s*. per quintal and reached a minimum in 1908.

The smell of European turpentine oil has been improved by treatment with oxidising agents, such as permanganate, persulphates, or chromic acid, or, better still, with hydrogen peroxide sodium peroxide, barium peroxide, or oxides of nitrogen.

By suitable application of Halphen's reagent (p. 381) or mercuric acetate, C. Grimaldi (1910) was able to detect adulteration with pine oil or resin oil.

transformed by oxidising agents into camphor and by ozone into the ozonide (Harries, 1910), these reactions establishing its constitution. **FENCHENE** is similar to camphene but is an optically inactive liquid, boiling at 158° to 160°; it resists the action of nitric acid, but not that of permanganate.

CAMPHANE, $C_{10}H_{18}$, forms white volatile crystals melting at 154° and boiling at 160°, and is obtained by reducing d- or l-bornyl iodide. It is optically inactive, and is the saturated hydrocarbon of the camphor nucleus.

HOMOLOGUES OF TERPENES. The most interesting lower homologue is **Hemiterpene or Isoprene**, C_5H_8 (*see* p. 90), which gives various terpenic polymerisation products, such as $(C_5H_8)_3$ (**Clovene, Cedrene, Caryophyllene**, &c.), $C_{20}H_{32}$ (**Colophene**), $C_{10}H_{16}$ (**Rubber**),[1] &c.

[1] RUBBER (*caoutchouc*) is obtained from the milky juice exuding when incisions are made in the stems of certain plants. The latter are mainly tropical trees (*Apocyneæ*, *Moraceæ*, *Euphorbiaceæ*, &c.; *Siphonia elastica*, more especially in Brazil, and *Urceola elastica* in Eastern India). According to Henri (1906–1908), the faintly alkaline latex contains the rubber, ready formed, in the form of minute emulsified drops (50 millions per c.c.), which are in continual movement, and of which this author was able to obtain a cinematographic representation; a coagulum is produced by acids, by salts of divalent metals (Ca, Mg, Ba, &c.), and less rapidly by salts of trivalent metals, &c., but not by alkalis. The conditions of coagulation, which are not identical with different varieties of latex, are in general related to the quality of the rubber yielded. The best quality (*Para rubber*) is obtained by drying superposed thin layers of fresh latex in a mould by means of hot gases until about a hundred layers, each about 0.5 mm. in thickness, are obtained. The commoner qualities are set by the heat of the sun, with addition of acid, water, formalin, or a trace of mercuric chloride; the electrolytic separation of rubber has also been suggested (Ger. Pat. 218,927 of 1908), but, according to Pahl (Ger. Pat. 237,789 of 1910) hydrofluoric acid or carbon dioxide gives the best results. The fundamental component of rubber, the hydrocarbon, $C_{10}H_{16}$, is mixed with varying quantities of a resin soluble in alcohol or in acetone; Para rubber contains less than 2 per cent. of resin, but the inferior qualities as much as 8 to 10 per cent. The removal of mineral substances and organic detritus is effected by manipulating, softening, and cutting the rubber in cold water, first in a kind of hollander (*see* Paper), then in a mechanical pulping machine and between rolls; the water is then removed and the rubber dried at 40° to 50°.

The consumption of rubber on a large scale began fifty or sixty years ago, after it had been found possible to render it unattackable by ordinary reagents and solvents and to keep it elastic even when exposed to the air and to heat. This is attained by *vulcanising* (suggested in 1839 by Goodyear and by Hancock), which consists in mixing sulphur with the rubber and heating in an oven or in a steam apparatus at 110° to 140°. Vulcanisation can also be carried out in the cold, by immersing the rubber in a mixture of sulphur chloride and carbon disulphide. The weighting materials or *fillers*, *e.g.* metallic oxides, kaolin, barytes, &c. (10 to 15 per cent.), are added with the sulphur. In place of sulphur chloride, which may give rise to a little hydrochloric acid, Bloch (Ger. Pat. 219,525 of 1908) has suggested hydrogen disulphide, H_2S_2, or trisulphide, H_2S_3, dissolved in acetone or carbon disulphide.

According to C. O. Weber and Henriques (1894), in vulcanisation in the cold, the excess of S_2Cl_2 may form compounds with the rubber varying in composition from $(C_{10}H_{16})_{24}$, S_2Cl_2 with 4.3 per cent. S, to $(C_{10}H_{16})_{24}$, $(S_2Cl_2)_{24}$ with 23·6 per cent. S.

E. Stern (1909) holds that the quantity of sulphur fixed is variable, while Hinrichsen (1910) maintains that the amount of S_2Cl_2 combined is constant. Ostwald (1910) explains vulcanisation as an *adsorption* phenomenon of the colloidal rubber, and assumes that the sulphur forms a series of reaction products, the first and last members of which cannot be isolated, and that the process is partly reversible.

By protracted vulcanisation of rubber with 60 to 75 per cent. of sulphur or sulphide and mixing in mineral substances (gypsum, chalk, inorganic colours, &c.), *ebonite* is obtained. (*Guttapercha* is similar to rubber but contains oxygen.)

Rubber has a brown or black colour and is insoluble in water when not vulcanised, and more or less soluble in chloroform, ether, petroleum ether, benzene, or carbon disulphide. Vulcanised rubber is almost insoluble in these substances, but dichloroethylene, $C_2H_2Cl_2$, forms an excellent and non-inflammable solvent.

With age, rubber (tubing, &c.) becomes hard and brittle, and cracks. According to Wo. Ostwald (Ger. Pat. 221,310 of 1908), it lasts longer if quinoline, aniline, dimethylaniline, &c., is used in its preparation.

Rubber is recovered from vulcanised waste by subjection of the latter, after removal of the impurities and comminution, to the action of steam under a pressure of 6 atmos. By this means a large part of the sulphur seems to be converted into sulphuric acid, which can be readily removed with water or soda. The residue is compressed into strips, but it is always an inferior product. There are now numerous patents, some of them fanciful for *devulcanising* rubber by means of alkaline solutions, phenols, naphthalene, aniline (Ger. Pat. 99,089), &c. In 1907 Tissier obtained good results by macerating used, finely divided rubber with double its weight of terpineol in a closed vessel at 120° to 150°, then diluting with 4 parts of benzene and decanting the solution from the impurities. The benzene is recovered by direct distillation and the terpineol by distillation in steam. In general, devulcanisation is based on depolymerisation of the vulcanised rubber where the sulphur is not united chemically with the rubber; it is almost impossible to eliminate the sulphur which is combined chemically. Old rubber, well devulcanised and then again vulcanised, seems to give a more resistant product but of lower quality. The United States import 10,000 tons of used rubber for "reclaiming". The Mitchell process is often used in America for obtaining rubber from old articles (boots, rubbered textiles, &c.), which are treated with sulphuric acid of 20° to 25° Bé., this destroying the textile fibres but not the rubber.

The *chemical constitution* of the hydrocarbon of rubber, $C_{10}H_{16}$, was determined by Harries (1905) by means of its *ozonide*, $C_{10}H_{16}O_6$, which decomposes into levulinic aldehyde, so that the hydrocarbon must be regarded as derived from an eight-carbon-atom ring (a ring never yet found in natural products);

$$\begin{array}{l} CH_3\cdot C\cdot CH_2\cdot CH_2\cdot CH \\ \;\;\;\;\;\;\;\; \| \; \| \\ \;\;\;\;\; CH\cdot CH_2\cdot CH_2\cdot C\cdot CH_3. \end{array}$$

In 1909 Harries obtained true artificial rubber by polymerising isoprene in presence of glacial acetic acid in sealed tubes at 100°: $(2C_5H_8)_x = (C_{10}H_{16})_x$, but the process is too expensive to be used industrially. The firm of Bayer (Elberfeld) also obtained artificial rubber from isoprene and from Erythrene C_4H_6 (*see* p. 90; *also* Ger. Pat. 235,423 and 235,686 of 1909 and Fr. Pat 425,582 of 1911), by prolonged heating in presence of benzene, &c., but this product is also very expensive; in consequence of this method of formation, the formula attributed

Other hydrocarbons related to the terpenes are: *ionene* and *irene*, two isomerides of the formula, $C_{13}H_{18}$, the ketones of which, $C_{13}H_{20}O$, are *irone* and *ionone*, *i.e.* the aromatic principle of iris root, having a marked violet smell.

IONONE (Artificial Essence of Violets) was prepared synthetically by Tiemann and Krüger in 1883 by shaking equal proportions of citral and acetone with barium hydroxide solution, extracting with ether and expelling the latter by evaporation.

The fraction of the residue boiling at 138° to 155° is **Pseudoionone**, which is transformed into the isomeric ionone by the action of dilute acid (Ger. Pat. 75,120). According to Ger. Pat. 113,672, the condensation may be effected by water in an autoclave at 170°, while in presence of sodamide it takes place at the ordinary temperature (Ger. Pat. 147,839). *See also* Ger. Pat. 138,939.

by Harries to the hydrocarbon is now contested. Various patents have recently been taken out for the preparation of *isoprene*, *dimethylbutadiene*, *erythrene*, &c., as prime materials for artificial rubber (Eng. Pats 29,566 and 29,277 of 1909). The Badische Anilin und Sodafabrik (Ludwigshafen) obtained rubber by heating isoprene and dimethylbutadiene (Fr. Pats. 417,170 and 417,768 and Eng. Pat 14,281 of 1910) in presence of alkali, which has a polymerising action. Harries (1911) showed that various isomeric artificial rubbers exist, with the generic formula $C_{10}H_{16}$, C_8H_{12}. Contrary to Weber's statement, Hinrichsen (1909) showed that the latex of rubber trees does not contain diterpenes, which polymerise to form rubber but that the latter exists ready formed in the latex.

The world's production of rubber was 52,190 tons in 1899; 59,750 in 1901; 68,500 in 1904; 73,680 in 1905; 75,300 in 1907, and about 80,000 tons (£30,000,000) in 1910–1911. The French East African possessions give 7000 tons; the French Congo 3000 and the Belgian Congo 6000. The total consumption in 1904 was distributed as follows: United States, 26,470 tons; Germany, 12,800 (about 15,600 in 1909); England, 10,000; France, 4130; Austria-Hungary, 1320; Holland, 1218; Belgium, 748 (increasing rapidly); Italy, 548 One-half of the world's output of rubber comes from Brazil, which produced 28,600 tons in 1902 and nearly 34,500 tons in 1908. Mexico exports rubber to the value of £1,280,000. The exports from Ceylon were 450 tons in 1908; 750 in 1909, and 1700 in 1910, while Abyssinia exported 9 tons in 1908 and 79 tons (£15,280) in 1909. A considerable part of the total output of rubber comes from Africa (Senegal, Madagascar, the Congo, the Cameroons, &c.), the exports being 16,000 tons in 1900 and 23,500 in 1906. The East Indies produce about 2000 tons per annum, but the cultivation of rubber is increasing rapidly. Brazil exported about 27,000 tons of rubber, at £60 per ton, in 1902; 31,600 tons in 1905; and 35,000 tons, valued at £1,720,000, in 1906 In Malacca the English have rapidly extended the rubber plantations, the exports being valued at £17,000 in 1900, and at £720,000 (1580 tons) in 1908, 1017 tons being exported in 1907. The number of rubber-producing trees was 27,500,000 in 1907, and 37,500,000 in 1908. The most suitable climate and soil for rubber are found at Malacca.

The areas under rubber in different countries in 1911 were as follow: Malacca, 170,000 hectares; Ceylon and Southern India, 110,000; Borneo, 35,000; Mexico, Brazil, and Africa, together, 45,000; German colonies, 20,000 The mean yield of rubber is calculated at 42 kilos per hectare in Ceylon and 38 in Samoa.

The Russo-American Rubber Company of St. Petersburg produced rubber articles to the value of £4,800,000 in 1907, £5,360,000 in 1908, and £5,800,000 in 1909.

In Germany there were 339 factories (with 12,500 employees) for making rubber and gutta-percha articles in 1895, and 100 factories, with 35,000 employees, a capital of £5,600,000, and an annual output valued at £10,000,000, in 1908. In 1904 Germany imported 17,407 tons of rubber of the value of £5,400,000, and exported 4569 tons, worth £1,400,000. In 1908 Germany imported more than 13,000 tons of raw rubber, 1500 tons of it from the German African colonies, especially the Cameroons; in 1910 the imports were about 10,000 tons

In Italy the firm of Pirelli and Co., founded in 1872, has two factories for the working of rubber, with a total capital of £600,000, an annual turnover of £640,000 (including submarine cables), and about 4000 operatives. A less important factory is that of the Italian company for the manufacture of rubber at Milan. Raw rubber imported into Italy pays no duty, but the manufactured product pays from £2 to £3 per quintal. The imports of raw rubber and gutta-percha amounted to 6688 quintals in 1904, 7669 in 1905, 1500 in 1908, and 18,800 (£980,000) in 1910; the exports, in the form of string, ribbon, and tubing, being 639 quintals in 1904, 1183 in 1905, and 109 in 1910 The total imports were 5715 quintals in 1904, 8061 in 1905, 2400 in 1908, and 2300 (£112,000) in 1910; and the tota exports, 3580 quintals in 1904, 4884 in 1905, 625 in 1908, and 1150 (£92,000) in 1910.

Belgium occupies 1900 workpeople in the rubber industry and France 9000 (in 1901).

The amount of rubber imported into England was 35,000 tons (£14,138,200) in 1909 and 43,500 tons(£26,096,790 together with 4800 tons (£1,136,500) of gutta-percha, in 1910.

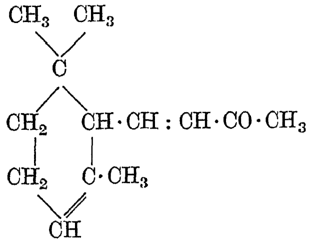
The imports of rubber to the United States were 40,500 tons (£19,600,000) in 1910 and 37,000 tons (£14,880,000) in 1911, in addition to 16,000 tons (£601,000) of waste rubber in 1910 and 8600 tons (£306,000) in 1911.

Gutta-percha resembles rubber, and is obtained mostly in Singapore and Borneo from a large tree, *Isonandra percha*. After purification and manipulation in hot water, it sets in the cold to a hard mass, soluble slightly in ether and alcohol and more readily in hot benzene, carbon disulphide, or chloroform. It is used as an electrica insulator and for making various articles

The *price* of raw rubber has increased rapidly from 320*s.* per quintal in 1850 to 448*s.* in 1890 and 664*s.* in 1907 (at Hamburg). The finer qualities of Para rubber cost 720*s.* in 1902, 1280*s.* in 1905, and 1280*s.* to 1600*s.* in 1909 Gutta-percha costs 360*s.* per quintal. It is estimated that the cost of native labour in the Congo district is not more than 120*s.* per quintal.

RUBBER SUBSTITUTES. Many of these have been prepared, but the only one of much practical importance is the so-called *factis*, of which two types are on the market: white and brown or black. The latter is made by boiling rape oil or linseed oil in an open vessel for two hours, cooling, and passing a current of air through it for thirty-six hours. It is then vulcanised by adding 2 per cent. of flowers of sulphur, heating for two hours at 140° adding a further 1 per cent. of sulphur, and raising the temperature to 150°, when it begins to rise White factis is obtained by treating the oil with 20 to 25 per cent. of sulphur chloride (free from dichloride); the energy of the reaction may be modified by adding the sulphur chloride dissolved in carbon disulphide. The mass is obtained in sheets or blocks by pouring it immediately on to cold metal plates or moulds. These substitutes are almost as elastic as rubber and are used to adulterate rubber, their price being 72*s.* to 96*s.* per quintal; they are insoluble in water or acid, but dissolve slightly in dilute alkali. They are distinguished from rubber by being saponifiable with alcoholic potash.

The constitution of synthetic ionone is:



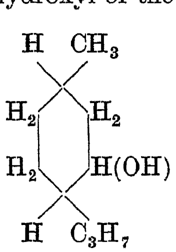
Ionone (100 per cent.) costs £152 per kilo, and *β-ionone*, £60; the 20 per cent. solutions are sold at one-fifth of these prices.

CAMPHORS

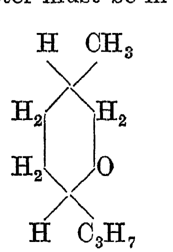
While the terpenes are liquids, the camphors are generally solid. They contain alcoholic or ketonic oxygen, and the principal ones with a single ring are: **Menthone**, $C_{10}H_{18}O$, and **Terpinol** with the same formula, while **Menthol** and **Carvomenthol** are $C_{10}H_{20}O$, and **Terpin** $C_{10}H_{20}O_2$. Among the camphors with complex rings are true **Camphor**, **Fenchone**, and **Carone**, $C_{10}H_{16}O$, and **Borneol**, $C_{10}H_{18}O$.

The camphors poorer in hydrogen and oxygen contain double linkings, form additive products, and are readily oxidised, while the others behave like saturated compounds.

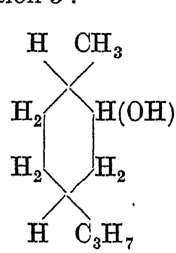
When reduced with sodium, the ketonic camphors yield the alcoholic camphors, which are converted into the former on oxidation. It is possible to pass from the camphors to the terpenes by way of the chlorides, and reduction of the alcoholic camphors often gives the terpene hydrocarbons. Thus, the **Terpane** (*hexahydrocymene*) can be obtained by reducing the **Terpanol** (*menthol*, $C_{10}H_{20}O$), which contains a hydroxyl or secondary alcoholic group, this being transformed by oxidation into the ketonic group with formation of **Terpanone** (*menthone*),[1] so that the hydroxyl should be in the ortho-position with respect to the CH_3 and C_3H_7 groups, as is shown below in the constitutional formulæ. On the other hand, since **Carvacrol**, $C_6H_3(\overset{2}{OH})(\overset{1}{CH_3})(\overset{4}{C_3H_7})$ (isomeric with carvone or carvol), of known constitution, gives on reduction a terpanol (*carvomenthol* with the hydroxyl in the position 2) different from that of menthol, the hydroxyl of the latter must be in position 3:



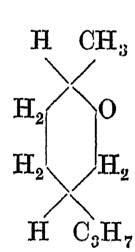
Menthol (terpanol), $C_{10}H_{20}O$



Menthone (terpanone), $C_{10}H_{18}O$



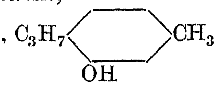
Carvomenthol $C_{10}H_{20}O$



Carvomenthone $C_{10}H_{18}O$

MENTHOL (3-Terpanol), $C_{10}H_{19} \cdot OH$, occurs in abundance in oil of peppermint, from which it can be obtained crystalline by cooling. It melts at 42°, boils at 213°, and has the strong odour of peppermint. The position of the OH is established by the fact that,

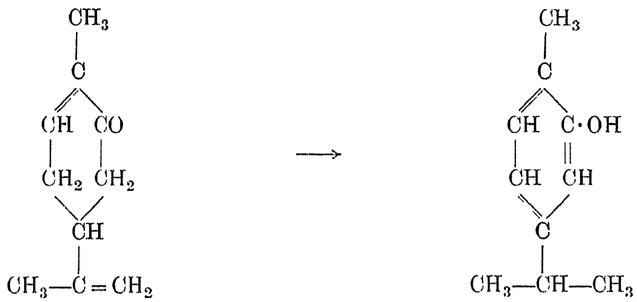
[1] Ciamician and Silber (1910) showed that, in alcoholic solution and under the action of light menthone is hydrolysed with formation of decoic acid, and an aldehyde isomeric with *citronellal* (p. 210)

with bromine in chloroform solution, *menthone* (which is the corresponding ketone, boiling at 207°, and having a strong smell of peppermint) gives dibromomenthone, and elimination of 2HBr from the latter gives thymol having the known constitution, ;

the CH_3 and OH are here undoubtedly in the meta-position, since elimination of the C_3H_7 by means of P_2O_5 yields m-cresol. When heated with copper sulphate, menthol yields cymene. Four isomerides of menthol are possible theoretically. It is used as an anæsthetic and as a disinfectant.

PULEGONE ($\Delta^{4(8)}$-Terpen-3-one), $C_{10}H_{16}O$, predominates in oil of pennyroyal (*Mentha pulegium*). It is a ketone boiling at 222°, and on reduction gives menthol, so that the carbonyl group is in position 3.

CARVONE (Carvol or Terpadien-2-one), $C_{10}H_{14}O$, is a ketone giving **Carvoxime**, $C_{10}H_{14}:NOH$, which exists in optical isomerides and is identical with nitrosolimonene. It forms the principal component of cumin oil, boils at 228°, and is converted into **Carvacrol**, $C_{10}H_{13}\cdot OH$, when heated with potash or phosphoric acid :

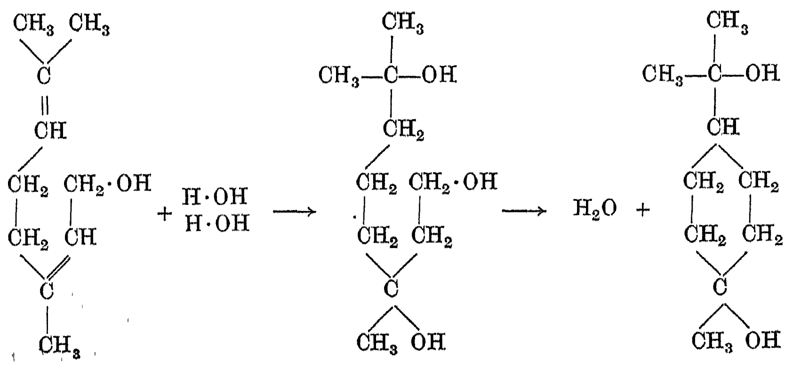


Carvone Carvacrol

TERPENOL ($\Delta^{4(8)}$-Terpen-1-ol), $C_{10}H_{18}O$, melts at 70°, and, like tetramethylethylene, forms a solid blue nitrosochloride, the double linking being in the 4(8)-position, between two tertiary carbon atoms.

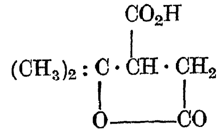
TERPINEOL (Δ^{1}-Terpen-8-ol), $C_{10}H_{18}O$, melts at 35°, boils at 218°, and is known in the form of various optically active isomerides. It has a pleasing odour of lily of the valley, lilac, and cyclamen, and occurs in ethereal oils. With sulphuric acid it forms terpin hydrate, which is also converted back into terpineol by sulphuric acid.

TERPIN (1 : 8-Terpandiol), $C_{10}H_{18}(OH)_2$. Terpin hydrate, $C_{10}H_{20}O_2,H_2O$, is slowly formed from oil of turpentine, $C_{10}H_{16}$, in contact with dilute nitric acid and alcohol. This crystalline hydrate melts at 117° and then loses 1 mol. of H_2O, anhydrous terpin distilling over at 258°. This is optically inactive and is not obtainable in active modifications, so that the presence of asymmetric carbon atoms is excluded. The hydrate is also obtainable from geraniol by the prolonged action of 5 per cent. sulphuric acid, $2H_2O$ being added at the double linkings :



Geraniol Terpin hydrate Terpin

Nitric oxide oxidises terpin, giving **Terebic Acid**, which has the known constitution:



so that the position 8 must be occupied by a hydroxyl; the other hydroxyl can only be in position 1, since otherwise an asymmetric carbon atom would be obtained.

CINEOL, $C_{10}H_{18}O$, has the constitution of terpin less H_2O, which is eliminated from the two hydroxyls, an atom of oxygen thus remaining united to the two carbon atoms 1 and 8. Cineol melts at $-1°$, boils at 176° and occurs in abundance in eucalyptus oil and in oil of wormseed.

FENCHONE, $C_{10}H_{16}O$. The dextro-form occurs in fennel oil and the lævo in thuja oil. It is a ketone similar to camphor and can be converted into **Fenchene**.

CAMPHOR (*ordinary camphor, laurel camphor*, or Japan Camphor), $C_{10}H_{16}O$, is the constituent which separates in the solid form from the essential oil of *Laurus camphora*, a tree which is cultivated in China, Japan, and Formosa, and grows well in Southern Europe (Italy).

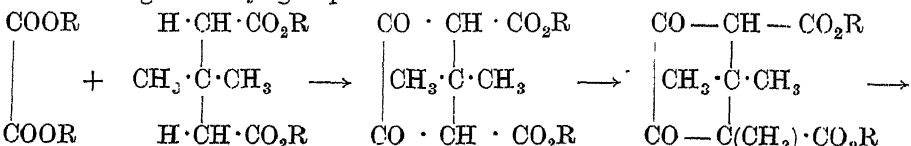
The wood (thirty to forty years old) is chopped up and boiled with water until the camphor floats at the surface; on cooling, the crude camphor sets to a solid mass, which can readily be separated. In some cases the camphor is distilled directly from the wood in a current of steam. The yield is about 1 kilo per quintal of wood. The crude product is refined by mixing with quicklime and charcoal and subliming at a gentle heat.

It is obtained thus as a white, crystalline, and not very hard mass, which has a characteristic odour, and partially sublimes at the ordinary temperature. It melts at 178°, boils at 207°, and has the sp. gr. 0·922–0·995 (the finer Borneo camphor has sp. gr. 1·10). In alcoholic solution it is more or less dextrorotatory, according to its origin, but *matricaria camphor* (from the leaves of feverfew, *Matricaria parthenium*) is lævo-rotatory.

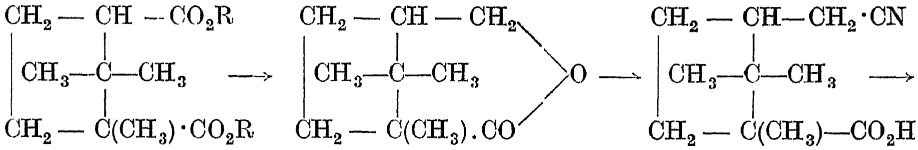
With iodine in the hot it forms carvacrol (*see above*), while oxidation with nitric acid gives **Camphoric Acid**, $C_8H_{14}(CO_2H)_2$, which exists in two active and two inactive forms. Further oxidation yields **Camphoronic Acid**, $C_9H_{14}O_6$, which gives trimethylsuccinic acid on dry distillation. When distilled with P_2O_5, camphor loses H_2O and forms cymene. On reduction with nascent hydrogen, ordinary camphor gives Borneol (*Borneo camphor*), $C_{10}H_{17}\cdot OH$, which melts at 208°, boils at 212°, and when oxidised gives ordinary camphor, which it strongly resembles.

Between 1860 and 1893 various constitutional formulæ for camphor were proposed by Kekulé, Armstrong, Bredt (1884), and G. Oddo (1891), the last of whom gave a formula which explained well all the reactions and properties observed up to that time. More and more acceptable constitutions were given by Widmann (1891), Collie (1892), Bouveault (1892), &c., and finally by Bredt (1893).

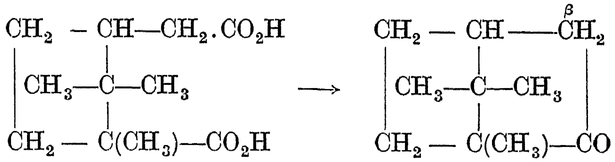
The *constitution* of camphor now seems to be definitely established as the result of various syntheses, especially that from ethyl oxalate and ethyl $\beta\beta$-dimethylglutarate, two compounds which are obtainable synthetically from their elements. The various stages in this synthesis are as follow, R indicating the alkyl group:



Ethyl oxalate — Ethy $\beta\beta$-dimethylglutarate — Ethyl diketoapocamphorate — Ethyl diketocamphorate



Ethyl camphorate Campholide Homocamphoric nitrile



Homocamphoric acid Camphor

This constitutional formula proposed for α-camphor by Bredt, although still contested, is the one generally accepted by chemists, since it corresponds best with most of the reactions of camphor. In 1911, Bredt and Hilbing prepared *β-camphor*, containing the CO group in the β-position, from *bornylene-carboxylic acid*; it melts at 182° and boils at 213·4°.

Camphor forms strongly rotating energetic sulphonic acids, *e.g.* $C_8H_{14}\left\langle\begin{matrix}CH\cdot SO_3H\\ |\\ CO\end{matrix}\right.$, which are able to resolve many racemic compounds into their active components.

Since many terpenes give camphor on oxidation, many attempts have been made to prepare *artificial camphor* from oil of turpentine.[1] The latter contains pinene, $C_{10}H_{16}$, which is readily convertible into borneol, $C_{10}H_{17}\cdot OH$, or isoborneol, this giving the inactive racemic compound corresponding with natural camphor on oxidation.

According to Ger. Pat. 134,553, when anhydrous turpentine is heated for a long time at 120° to 130° with dry oxalic acid, a mixture of camphor with pinyl formate and oxalate is obtained; after washing with water, the latter are hydrolysed with alkali and the resultant borneol converted into camphor by oxidation with dichromate and sulphuric acid.

At Monville, near Rouen, a factory was erected in 1906 to manufacture artificial camphor by the process described in Fr. Pat. 349,896 (of Béhal, Magnier, and Tissier, and similar to U.S. Pat. 779,377): A mixture of oil of turpentine and salicylic acid is heated and, after elimination of the excess of the reagents, the isoborneol ether is hydrolysed to a mixture of borneol and isoborneol. Another factory, near Calais, utilises Schering's method (Fr. Pat. 341,513), already in use on a large scale in Berlin, and also applied in a factory established in 1909 in Finland.

According to Fr. Pat. 349,852, pinene hydrochloride is first prepared and then heated under pressure with lead acetate in acetic acid solution, thus giving camphene, which with permanganate forms camphor; or treatment of the pinene hydrochloride with a formate gives the formic ester of borneol, which can be readily hydrolysed. The final oxidation to obtain camphor is carried out in various ways: by oxidising the borneol, in benzene or petroleum ether solution, with aqueous alkaline permanganate (Ger. Pat. 157,590), or by means of ozone, air, or chlorine water (*see* Eng. Pat. 28,036 of 1907 and Ger. Pats. 166,722

[1] It has been pointed out that a difficulty in the way of the further development of the present artificial camphor industry may be the excessive price of oil of turpentine, this having risen from 56*s*. per quintal in 1900 to 96*s*. in 1906; these conditions might easily be aggravated by the formation of a trust. Further, the demand for camphor may diminish in the future, since substitutes are continually being found capable of replacing it in celluloid, which up to the present has consumed about two-thirds of the total camphor produced. The fact that natural camphor—almost entirely monopolised by the Japanese Government—can be sold, without loss, at 144*s*. per quintal constitutes a menace to the future of artificial camphor, which could never be sold at that price and depends on a raw material the price of which cannot be regulated. In addition to the 70 per cent. absorbed in the manufacture of celluloid, natural camphor is used for explosive powder and guncotton (2 per cent.), for pharmaceutical preparations (13 per cent.) and for various other purposes (15 per cent.)

and 154,107), or by oxidising isoborneol in aqueous acid solution with permanganate (Ger. Pat. 197,161 of 1906).

Camphor was obtained by A. Hesse by means of the Grignard reaction, and it is also formed by fusing borneol with finely divided nickel (1911).

Natural camphor may be distinguished from the artificial product by mixing it intimately with an equal weight of chloral hydrate: the former gives a syrupy mass, but the latter does not liquefy. Camphor is used in pharmacy, for fireworks and nightlights and, in large quantities, in the manufacture of *celluloid*[1] and for rendering explosives insensitive to shock. The price of camphor varies somewhat, and during the Russo-Japanese War rose considerably: it is usually about £24 per quintal. The cost price of artificial camphor seems to be about 4*s*. per kilo.

The production of camphor in Japan and Formosa (State monopoly) amounted to about 3,500,000 kilos (three-fourths in Formosa) in 1906, and to 4,300,000 kilos, 2,000,000 kilos being exported (two-thirds to Havre, London, and Hamburg, and one-third to America), in 1907. After the war with Russia, Japan, with her monopoly of the production of camphor, tried to raise the price. From about 2*s*. 5*d*. per kilo in 1903 it became 4*s*. 5*d*. in 1906 and 1907. At the same time large plantations were laid out in Formosa, 1,300,000 trees being planted in 1907, about 1,400,000 in 1908, and more than 5,000,000 in 1909. The rise in price caused increased production of artificial camphor in Europe, and, owing to this competition, the price fell again to 2*s*. per kilo at Japanese ports in 1911. The exportation from Japan, which had fallen to 1,500,000 kilos in 1908, rose to 2,430,000 kilos in 1909, but steps are now being taken to regulate the output so that the price may not be lower than the actual cost of production, this being about 1*s*. 9*d*. in Formosa and 2*s*. 10*d*. for camphor produced in Japan.

In 1906 Japan prepared 1,600,000 kilos and in 1907 more than 3,000,000 kilos of *camphor oil*.

An association was formed in the United States in 1908 to sterilise the camphor trees of Florida and Texas, the system of cultivation being thus improved.

The exports of camphor from China were as follow: 120 quintals in 1902; 660 in 1903; 725 in 1904; 2450 (£60,000) in 1905; 6000 (£220,000) in 1906; 11,600 (£280,000) in 1907—the total output being 16,000 quintals; 4820 (£108,000) in 1908, the total output being 8000 quintals; £100,000 worth in 1909 and still less in 1910. Trees have been used up in China without new plantations, which require 40 years before giving good trees, being established. Continuance of this procedure will result in the complete destruction of camphor trees in China in seven or eight years.

England imported nearly 387 tons of camphor in 1899; France about 546 tons and Germany more than 1000 tons (£320,000) in 1903. The average price of camphor in Hamburg was 141*s*. in 1881–1885, 181*s*. in 1886–1890, 235*s*. in 1891–1895, 268*s*. in 1896, and 200*s*. in 1897. It now tends to increase owing to the Japanese monopoly.

The United States imported in 1910 1700 tons (£226,000) of crude *natural camphor*, and in 1911 1150 tons (£165,000), besides 160 tons (£23,000) of purified and artificial camphor. The exports of celluloid and articles made therefrom amounted to £286,800 in 1910 and £420,200 in 1911.

The *world's consumption* of camphor is about 5000 to 6000 tons, almost all placed on the market by Japan, which has collected Chinese camphor since the monopoly there came to an end in 1904.

Camphor is not produced in Italy, where, however, according to the excellent-mono-

[1] Celluloid is obtained by mixing nitrocellulose and camphor in the following manner: well-stabilised powdered, and partially dried collodion-cotton (with 10 to 11 per cent N.; see p. 239) is soaked in alcohol in a covered centrifuge, then gelatinised with alcohol and one-third or one-fourth of its weight of camphor, coloured, if necessary, homogenised between rolls and then formed into dense, compact blocks by pressing while hot. It is then ready to be cut, sawn, compressed, polished, &c., its marked plasticity when hot being utilised in working it. It is a homogeneous, transparent, colourless, or yellowish substance without taste and of sp. gr. 1·37. If sufficiently dry it is odourless, but, when rubbed or heated, it develops a slight smell of camphor. It is a very bad conductor of heat and electricity, and its elasticity is about equal to that of ivory.

Celluloid is used for making toys, balls, combs, walking-stick handles, tortoiseshell objects (substitutes for tortoiseshell, amber, ebonite, &c.), films, &c. It has the disadvantage of burning rapidly and energetically (without exploding) when brought into contact with an ignited or incandescent body. If the collodion-cotton used is well stabilised, celluloid will withstand a temperature of 125° or even higher. It can be charged with mineral substances to render it less inflammable and heavier.

graph presented by Giglioli at the International Congress of Applied Chemistry at Rome (1906), it could be produced advantageously on a large scale. Italian requirements are met by the importation of 20 to 25 tons per annum of refined camphor from Germany at a price of 280*s*. per quintal prior to 1898, 400*s*. after 1902, and 480*s*. after 1908 ; the import duty is 20*s*. per quintal. Italy imported 1000 quintals of celluloid in 1906, 2407 in 1909, and 4267 (£102,410) in 1910.

The value of the imports of celluloid into Japan were: £48,000 in 1905, £80,000 in 1906, £30,000 in 1907, and £60,000 in 1908. The import duty is £4 per quintal for celluloid in strips or in the crude state, and 40 per cent. for manufactured articles. Two large celluloid factories erected in Japan in 1908 produce annually 500,000 kilos, 300,000 kilos for exportation, and the rest for home consumption, this being previously supplied by importation from Germany (five-sixths) and England (one-sixth). In three large centres (Neckaren, Troisdorf, and Eilenburg), Germany produces annually about 5,500,000 kilos of celluloid of the value of £1,360,000.

P. CONDENSED BENZENE NUCLEI

DIPHENYL AND ITS DERIVATIVES

DIPHENYL, $C_6H_5 \cdot C_6H_5$, or , is formed by treating an ethereal solution of bromobenzene with sodium (Fittig), by the transformation of hydrazobenzene, or by diazotising benzidine and decomposing the resultant product. It can also be obtained by passing benzene vapour through a red-hot tube.

It forms colourless crystals melting at 71° and boiling at 254°, and is soluble in alcohol and in ether. On oxidation with chromic acid, it gives benzoic acid, its constitution being thus confirmed.

Of *monosubstituted* products of diphenyl, three isomerides are possible, corresponding with the o-, m-, and p- positions with respect to the carbon joined to the second nucleus. Disubstituted derivatives exist in numerous isomeric forms, as the substitution may occur in only one nucleus or in both ; in general, however, the substituents enter preferably the para-positions.

BENZIDINE (*p* : *p*-Diaminodiphenyl), $NH_2 \cdot C_6H_4 \cdot C_6H_4 \cdot NH_2$. Nitration of diphenyl yields p : p-dinitrodiphenyl, which, when reduced with zinc dust in alkaline solution, gives benzidine. The latter may also be obtained by electrolysis of nitrobenzene ; *see also* Ger. Pat. 122,046, according to which azobenzene is electrolysed in hydrochloric acid solution in presence of stannous chloride.

When pure, benzidine forms colourless scales melting at 122° and then subliming. It dissolves slightly in cold water, but readily in hot water, ether, or alcohol. It is a diacid base and gives a sulphate, $C_{12}H_8(NH_2)_2,H_2SO_4$, almost insoluble in water.

It is largely used in making *substantive* dyestuffs (such as *Congo red* and *chrysamine*, which dye cotton without mordants), being first diazotised and then combined with naphthylamine or naphthalenesulphonic acids.

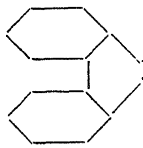
Crude benzidine costs about 5*s*. per kilo and the pure product 48*s*. The crude sulphate in paste (63 per cent.) costs 2*s*. per kilo and the pure 36*s*.

A higher homologue of benzidine is *o*-Tolidine, $C_{12}H_6(CH_3)_2(NH_2)_2$, which melts at 128°, and the diazo-compound of which combines with naphthionic acid to form a red substantive dyestuff, *benzopurpurin 4B*. The dimethoxy-compound, $(O \cdot CH_3)_2$, of tolidine is *dianisidine*, which with α-naphthol-α-sulphonic acid forms *benzoazurin G* (substantive blue).

CARBAZOLE, $\begin{array}{l} C_6H_4 \\ | \\ C_6H_4 \end{array}\!\!\!>\!NH$, is found in coal-tar, and can be obtained

synthetically by distilling o-aminodiphenyl over red-hot lime or by gently heating diphenylamine vapour.

The unions of the nitrogen with the two phenyl groups are in the diortho-positions,



so that carbazole may be regarded as a pyrrole derivative (*see later*). It forms colourless scales melting at 238° and readily subliming, and it dissolves in concentrated sulphuric acid, giving a yellow coloration.

From diphenyl can be derived. four isomeric **Dihydroxydiphenyls**, $C_{12}H_8(OH)_2$; the **Diphenylsulphonic Acids**; **Diphenyl Oxide**, $(C_6H_4)_2O$; **Hexahydroxydiphenyl**, $C_{12}H_8(OH)_6$ (the. mother-substance of cærulignone); and the **Diphenylcarboxylic Acids** (the di-p-acid is a white powder, insoluble in water, alcohol or ether; the di-o-acid is **Diphenic Acid**, $CO_2H \cdot C_6H_4 \cdot C_6H_4 \cdot CO_2H$, m.pt. 229°) which give diphenyl when heated with lime.

2. DIPHENYLMETHANE AND ITS DERIVATIVES

These compounds may be obtained by condensing either 2 mols. of benzene (or its homologues) with one of methylene chloride, or 1 mol. of benzyl chloride (or benzoyl chloride) with one of benzene (or its homologues or derivatives) in presence of aluminium chloride:

$$2C_6H_6 + CH_2Cl_2 = 2HCl + C_6H_5 \cdot CH_2 \cdot C_6H_5$$
$$C_6H_3 + C_6H_5 \cdot CH_2 \cdot Cl = HCl + C_6H_5 \cdot CH_2 \cdot C_6H_5.$$

Condensation of 2 mols. of benzene with aldehydes (Baeyer) or 1 mol. of an aromatic aldehyde with one of benzene (V. Meyer) under the influence of concentrated sulphuric acid (ketones, phenols, tertiary anilines, &c., also act similarly):

$$2C_6H_6 + CH_3 \cdot CHO = H_2O + CH_3 \cdot CH(C_6H_5)_2$$
$$C_6H_6 + C_6H_5 \cdot CH_2 \cdot OH = H_2O + C_6H_5 \cdot CH_2 \cdot C_6H_5.$$

DIPHENYLMETHANE, $C_6H_5 \cdot CH_2 \cdot C_6H_5$, forms white crystals melting at 26° and boiling at 262°, has a smell of oranges and is soluble in alcohol or in ether. It is obtained synthetically (*see above*). With water at 150°, its bromo-derivative, $CHBr(C_6H_5)_2$, is converted into **Benzhydrol** (*diphenylcarbinol*), $(C_6H_5)_2CH \cdot OH$, which is also obtained on reducing benzophenone.

p-**Diaminodiphenylmethane**, $CH_2(C_6H_4 \cdot NH_2)_2$, and **Tetramethyldiaminobenzhydrol**, $OH \cdot CH[C_6H_4 \cdot N(CH_3)_2]_2$, are used in the preparation of dyestuffs.

BENZOPHENONE (Diphenylketone), $C_6H_5 \cdot CO \cdot C_6H_5$ (*see* p. 572).

o-**DIHYDROXYBENZOPHENONE**, $[C_6H_4(OH)]_2CO$, by the elimination of a molecule of water from the two hydroxyls, gives **Xanthone**, $C_6H_4{<}\substack{CO\\O}{>}C_6H_4$. *p*-**Dihydroxybenzophenone** is obtained from anisaldehyde, so that the hydroxyl groups must be in the para-positions. **Trihydroxybenzophenone** is formed by the condensation of benzoic acid with pyrogallol in presence of zinc chloride. It is used in dyeing under the name *alizarin yellow C* (*see* Dyestuffs).

Other higher derivatives of diphenylmethane are as follow:

as-**DIPHENYLETHANE** (*see later* symm.dibenzyl) is liquid and is formed from paraldehyde and benzene (*see above*). **Benzilic Acid** (*diphenylglycollic acid*), $(C_6H_5)_2C(OH) \cdot CO_2H$, is a solid and is obtained by the action of KOH on benzil; by reduction with HI it gives **Diphenylacetic Acid**, $(C_6H_5)_2CH \cdot CO_2H$.

Tolylphenylmethane, $C_6H_5 \cdot CH_2 \cdot C_6H_4 \cdot CH_3$, exists in several isomeric forms.

Tolyl Phenyl Ketones, $C_6H_5 \cdot CO \cdot C_6H_4 \cdot CH_3$. The stereoisomeric oximes of these ketones were employed by Hantzsch in developing the stereochemistry of nitrogen (*see* pp. 20, 210, and 306).

Benzoylbenzoic Acids, $C_6H_5 \cdot CO \cdot C_6H_4 \cdot CO_2H$: the ortho-acid gives anthraquinone when heated at 180° with P_2O_5.

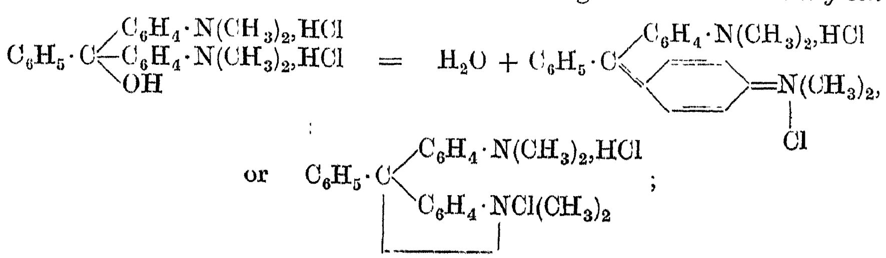
FLUORENE (**Diphenylenemethane**), $\left.\begin{array}{l} C_6H_4 \\ | \\ C_6H_4 \end{array}\right> CH_2$, is found in coal-tar, and is formed on heating diphenylmethane vapour. It melts at 113°, boils at 295°, and forms scales showing a violet fluorescence.

3. TRIPHENYLMETHANE AND ITS DERIVATIVES

These are prepared synthetically by processes analogous to those used for diphenylmethane, but under such conditions as to lead to the condensation of three benzene nuclei in the methane molecule. The action of chloroform on benzene in presence of $AlCl_3$ gives **TRIPHENYLMETHANE** (m.pt. 93°; b.pt. 359°):

$$CHCl_3 + 3C_6H_6 = 3HCl + CH(C_6H_5)_3.$$

The condensation of benzaldehyde and dimethylaniline yields **Tetramethyldiaminotriphenylmethane**, $C_6H_5 \cdot CH[C_6H_4 \cdot N(CH_3)_2]_2$, which is a *leuco-base* (*see* Dyestuffs) of malachite green; phenols, &c., condense similarly. When this colourless leuco-base is oxidised with PbO_2 and HCl, it gives **Tetramethyldiaminotriphenylcarbinol**, $C_6H_5 \cdot C(OH)[C_6H_4N(CH_3)_2]_2$ which is also a colourless base and forms colourless salts. When, however, these salts are heated in solution, they lose water and form an intense green *colouring-matter*, the double salt of this with zinc chloride or oxalate being known as *malachite green*:



on reduction, the colouring-matter (+ 2H) gives the leuco-base again.

PARAROSANILINE is obtained by oxidising 1 grm.-mol. of p-toluidine and 2 grm.-mols. of aniline with arsenic acid or nitrobenzene. The methyl of the toluidine furnishes the carbon atom for the methane nucleus:

$$CH_3 \cdot C_6H_4 \cdot NH_2 + 2C_6H_5 \cdot NH_2 + 3O = 2H_2O + OH \cdot C \begin{cases} C_6H_4 \cdot NH_2 \\ C_6H_4 \cdot NH_2 \\ C_6H_4 \cdot NH_2 \end{cases} \text{(base).}$$

With acids, this base gives a red colouring-matter which is precipitated by alkali. When reduced with zinc and hydrochloric acid it yields *paraleucaniline*, $HC(C_6H_4 \cdot NH_2)_3$, in colourless crystals which give the coloured base again on oxidation.

Elimination of the amino-groups by diazotisation leads to *triphenylmethane*, while nitration of the latter, followed by reduction, gives paraleucaniline, which yields *triaminotriphenylcarbinol* on oxidation. When treated with acids the latter loses H_2O, giving the colouring-matter:

$$OH \cdot C \begin{cases} (C_6H_4 \cdot NH_2)_2 \\ C_6H_4 \cdot NH_2,HCl \end{cases} = H_2O + CCl \begin{cases} (C_6H_4 \cdot NH_2)_2 \\ C_6H_4 \cdot NH_2 \end{cases}$$

ROSANILINE is formed by oxidising a mixture of o- and p-toluidines and aniline with arsenious anhydride, mercuric nitrate, or nitrobenzene, the carbon of the methane nucleus being furnished in this case also by the p-toluidine :

$$C_6H_4\left\langle\begin{array}{l}CH_3\\NH_2\end{array}\right. (p) + C_6H_4\left\langle\begin{array}{l}CH_3\\NH_2\end{array}\right. (o) + C_6H_5{\cdot}NH_2 + 3O =$$

$$2H_2O + OH{\cdot}C\left\langle\begin{array}{l}C_6H_4\left\langle\begin{array}{l}CH_3\\NH_2\end{array}\right. (o)\\(C_6H_4{\cdot}NH_2)_2\end{array}\right.$$

Rosaniline hydrochloride (with 1 HCl) or *fuchsine* forms crystals with a green metallic lustre, while the aqueous solution is red owing to the presence of the monovalent cation, $C_{19}H_{18}N_3$, the salt being almost completely ionised.

All fuchsine salts, at the same dilution, give the same absorption spectrum, as they contain the same cation.

If 3HCl are combined, the salts become yellow (yellow trivalent cation) ; indeed, with excess of HCl fuchsine is almost decolorised, although in dilute solution the red cation is again formed by dissociation.[1]

Replacement of the hydrogen atoms of the amino-groups by alkyl groups gives various colouring-matters, the intensity of the violet colour increasing with the number of methyl groups.

Pentamethylpararosaniline is the *methyl violet* of commerce.

ROSOLIC ACID and **AURIN** are the phenolic compounds corresponding with rosaniline and pararosaniline, from the diazo-compounds of which they are obtained by boiling with water :

$$C\left\langle\begin{array}{l}C_6H_3(OH){\cdot}CH_3\\C_6H_4{\cdot}OH\\C_6H_4:O\end{array}\right. \qquad\qquad C\left\langle\begin{array}{l}(C_6H_4{\cdot}OH)_2\\C_6H_4:O\end{array}\right.$$

Rosolic acid — Aurin

They are colouring-matters of an acid character and of but little importance and they form dark red prisms with a greenish, metallic reflection.

PHTHALOPHENONE, $C\left\langle\begin{array}{l}C_6H_5\\C_6H_5\\C_6H_4{\cdot}CO\end{array}\right.$ (with C and CO linked through O), may be regarded as a derivative of phthalic acid (*see* p. 580) or of triphenylmethane.

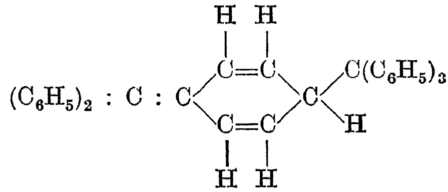
It is the anhydride of triphenylcarbinol-o-carboxylic acid, $C(OH)(C_6H_5)_2(C_6H_4{\cdot}CO_2H)$, and is obtained by heating phthalyl chloride with benzene in presence of aluminium chloride. It forms scales melting at 115° and dissolves in alkali giving a salt of the acid, the latter not being obtainable in the free state. Its phenolic derivatives are the *phthaleins* (*see* p. 581).

HEXAPHENYLETHANE, $(C_6H_5)_3C.C(C_6H_5)_3$, is of some interest theoretically, as its molecule was at first regarded as $C(C_6H_5)_3$ (Triphenylmethyl) and was

[1] It is commonly thought that in the hydrochloride the chlorine is joined to the amino-group and not to the carbon of the methane, since, as Tortelli showed (1895), all the chlorine is precipitable by silver nitrate ; the compound is hence a salt and not an ether. It cannot, however, be denied that there are compounds, such as *triphenylmethyl chloride*, $(C_6H_5)_3C{\cdot}Cl$, which behave similarly, being hydrolysable by water and then completely precipitable by silver nitrate. Then, too, *methyl iodide* is hydrolysed by water alone to the extent of 0·6 per cent. in forty-three hours, whilst in the presence of silver nitrate 96 per cent. of the iodide is hydrolysed in the same time. It is hence more accurate to state that, after hydrolysis, these ethereal compounds behave like salts.

Rosenstiehl maintains that every double decomposition between *salts* (especially organic) is preceded by hydrolysis, and those salts and ethereal compounds which hydrolyse slowly he calls *bradolytes*, and those which hydrolyse rapidly, *stenolytes*.

looked upon as the first example of an organic compound containing trivalent carbon. But cryoscopic examination shows that it has the doubled molecular weight, and hence indicates the constitution $(C_6H_5)_3C \cdot C(C_6H_5)_3$. It was prepared by Gomberg by the action of zinc on triphenylchloromethane, and is a solid, stable substance which, in solution, has a yellow colour and becomes unstable owing to its great power of reacting; with the oxygen of the air it forms a peroxide, $(C_6H_5)_3 \cdot C \cdot O \cdot O \cdot C(C_6H_5)_3$. On account of the facility with which it forms additive products, hexaphenylethane is regarded by some as having in solution the constitution:



An analogous compound is **Pentaphenylethane**, $(C_6H_5)_3C \cdot CH(C_6H_5)_2$, stable at the ordinary temperature but not in the hot.

4. DIBENZYL AND ITS DERIVATIVES

The constitution of these compounds is shown by their methods of synthesis and by the fact that they all yield benzoic acid on oxidation.

DIBENZYL (*symm.* Diphenylethane), $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot C_6H_5$, is obtained from benzyl chloride and sodium:

$$2C_6H_5 \cdot CH_2 \cdot Cl + Na_2 = 2NaCl + C_6H_5 \cdot CH_2 \cdot CH_2 \cdot C_6H_5;$$

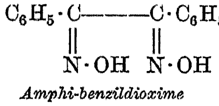
it melts at 52°.

STILBENE (*symm.* Diphenylethylene), $C_6H_5 \cdot CH : CH \cdot C_6H_5$, melts at 125°, and is obtained from benzal chloride (benzylidene chloride) and sodium. Owing to its double linking, it can unite with two atoms of Br, which can be eliminated as HBr by treatment with alcoholic potash, the resulting product being **TOLANE** (Diphenylacetylene), $C_6H_5 \cdot C \vdots C \cdot C_6H_5$, melting at 60°, and behaving like an acetylene derivative.

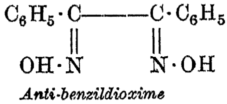
p-**DIAMINOSTILBENE**, $NH_2 \cdot C_6H_4 \cdot CH : CH \cdot C_6H_4 \cdot NH_2$, is used, especially in the form of the corresponding sulphonic acids, for the preparation of various substantive dyestuffs.

BENZOIN, $C_6H_5 \cdot CH(OH) \cdot CO \cdot C_6H_5$, is formed by oxidising **HYDROBENZOIN**, $C_6H_5 \cdot CH(OH) \cdot CH(OH) \cdot C_6H_5$, which is obtained by treating benzaldehyde with sodium amalgam. Benzoin exists in two stereoisomeric modifications, melting at 138° and 119°. It reduces Fehling's solution even in the cold (giving benzil) and forms a phenylosazone, since it contains, like the sugars, the group $\cdot CO \cdot CH(OH)$.

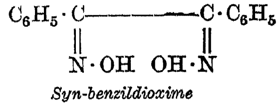
BENZIL, $C_6H_5 \cdot CO \cdot CO \cdot C_6H_5$, is a yellow diketone and forms three benzildioximes (*see* pp. 22, 210, and 572):



Amphi-benzildioxime



Anti-benzildioxime



Syn-benzildioxime

When heated with alcoholic potash, benzil combines with H_2O, giving benzylic acid:

$$C_6H_5 \cdot CO \cdot CO \cdot C_6H_5 + H \cdot OH = (C_6H_5)_2C{<}^{CO_2H}_{OH}.$$

DESOXYBENZOIN, $C_6H_5 \cdot CH_2 \cdot CO \cdot C_6H_5$, is obtained from phenylacetyl chloride, $C_6H_5 \cdot CH_2 \cdot CO \cdot Cl$, and benzene in presence of aluminium chloride, and also from benzoin and benzil. It melts at 55° and gives dibenzil when reduced with hydriodic acid.

HEXABENZYLETHANE, $(C_6H_5 \cdot CH_2)_3C \cdot C(CH_2 \cdot C_6H_5)_3$, was prepared by F. Schmerda (1909) by heating tribenzylcarbinol with hydriodic acid in a sealed tube at 200°, the product being shaken with bisulphite, extracted with ether and the latter distilled off. It forms a yellowish crystalline mass which is recrystallised from acetone and glacial acetic acid; it melts at 80° to 81°. From the mother-liquor dibenzyl is obtained.

5. NAPHTHALENE AND ITS DERIVATIVES

NAPHTHALENE, $C_{10}H_8$, occurs in abundance in crude illuminating gas and in coal-tar. When the latter is distilled (*see* p. 526 *et seq.*), the naphthalene is obtained from the portions distilling between 170° and 230° and by redistilling the residues of the oils from which the carbolic acid has been extracted with caustic soda, care being taken to surround the condenser coils with hot water to prevent stoppages.

The first separation of the naphthalene from the crude oils yielded at various stages of the distillation is effected by cooling in large tanks, crystallised naphthalene separating out.

The oily impurities of the crystals are removed in a hydraulic press with heated plates. Attempts have been made to centrifuge the crude naphthalene, but even when this is steamed in the centrifuge, the residual product is always very impure and unsuitable for distillation or sublimation. In consequence of this, use has been made of hydraulic presses with horizontal rods and vertical plates heated by steam, but these give insufficient pressure and too much waste, and require too much time and attention. The best results are given by presses with vertical columns and ring plates (similar to the presses described on p. 392), which work continuously and readily attain a pressure of 102 kilos per square centimetre with a diminished consumption of steam. Nowadays hydraulic presses with perforated steel bells are used—similar to those used for oily seeds—and in 10 hours each of these can effect 30 compressions of 100 kilos; when several presses are worked, hydraulic accumulators (*see* p. 393) are used. If well pressed, naphthalene has the mean solidifying point 78·6° and 95·5 per cent. of it distils between 216·5° and 218·5°. Attempts have been made to purify naphthalene with a solution of resin soap, but such a method is too expensive (a centrifuged naphthalene containing 7 per cent. of oil gives, with 5 per cent. of colophony and the corresponding quantity of caustic alkali solution, 85 per cent. of pure naphthalene with the solidifying point 78·8°). The compressed naphthalene is purified further in metal vessels with conical bases and fitted with stirrers (sometimes with air-jets). In these the molten naphthalene is agitated for 15 minutes with 5 per cent. of sulphuric acid of 50° Bé (already used once) to dry the mass somewhat and free it from pyridine compounds; after removal of this acid, the mass is shaken successively with 5 to 6 per cent. of sulphuric acid of 60° Bé. for 30 minutes, 4 per cent. of hot water, 4 per cent. of caustic soda solution of 19° Bé. (already used once), and, finally, 2 per cent. of hot water. After settling and removal of the water as far as is possible by decantation, the naphthalene is distilled in large stills holding 100 to 150 quintals and furnished with a rectifying column 2 to 3 metres high. Water distils over first and then pure naphthalene, which is collected in metal boxes, allowed to crystallise in moulds and granulated by means of a crusher; the solidifying point is then 70·7°, while 97·5 per cent. distils between 216·6° and 218°. A purer product, in the form of large, shining scales, can be obtained by *sublimation* (instead of distillation) in an open vessel, *a* (Fig. 419), having an area of 2 to 3 cu. metres and covered with an inclined wooden plane leading to a large wooden chamber, 20 to 25 cu. metres in capacity. The naphthalene is heated by a pressure steam-coil

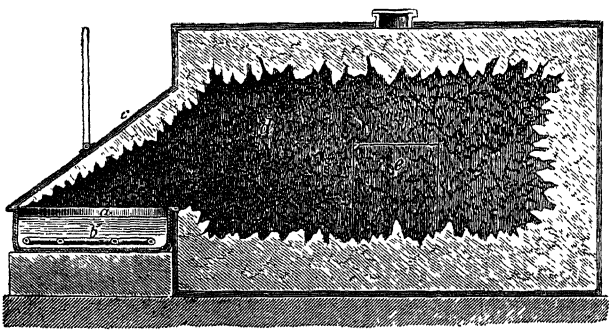


FIG. 419.

and sublimes and condenses in the large chamber, forming on the walls a thick layer of shining, white scales of pure naphthalene. In order to avoid loss and to obtain continuous working, the naphthalene is introduced into long cylindrical boilers, bricked in like steam boilers and connected with a large wooden chamber (350 cu. metres), which has a base fitted with conical outlets leading to sacks for catching the naphthalene as it becomes detached from the walls (these are knocked from time to time). In this way 70 kilos of pure naphthalene are obtained per 12 hours for each 100 cu. metres of capacity.

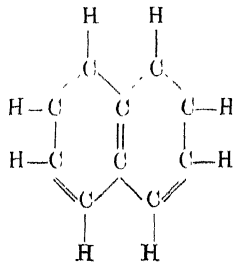
Pure naphthalene forms shining scales melting at 79·6° and boiling at 218°. It is insoluble in water, but dissolves readily in boiling alcohol or in ether ; it volatilises even at the ordinary temperature and distils readily in steam.

Naphthalene is used in large quantities in the preparation of various dyestuffs (eosin, indigo, Martius' yellow, tropæolin, Biebrich scarlet, croceine scarlet, &c.), phthalic acid, lampblack, varnishes, and cart-grease, and is employed also as an antiseptic and as a preventative of moth in clothes. For some time it has been mixed with camphor in order to render *celluloid* less inflammable and less explosive.

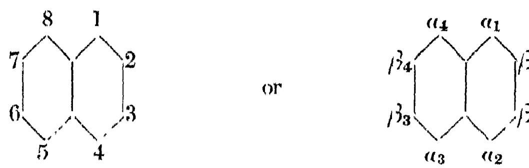
Crude naphthalene costs 11*s.* to 12*s.* per quintal, while the pure white scales are sold at 16*s.*, pure in tapers at 17*s.* 6*d.*, and chemically pure at 80*s.* per quintal. In 1910 Italy imported 371 quintals of naphthalene, of the value of £386 (in 1907, 42 quintals), and exported 2214 quintals (£2200) ; the production in Italy was 8600 tons (£71,880) in 1908. In 1909 Germany imported 77,445 and exported 63,544 quintals.

England exported 3650 tons of naphthalene, of the value of £28,110, in 1911.

Constitution of Naphthalene. The following structural formula is attributed to naphthalene :

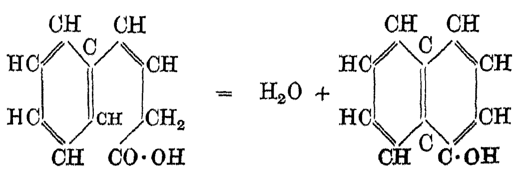


and to indicate the positions occupied by groups replacing the hydrogens in derivatives the carbon atoms are numbered or lettered with Greek letters, thus :

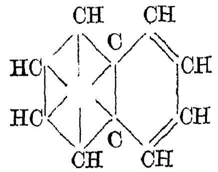


That the two nuclei are united by means of two carbon atoms in the ortho-position is shown by the fact that oxidation of naphthalene in such a way as to destroy one of the nuclei results in the formation of phthalic acid, which is known to contain two carboxyl groups in adjacent positions.

Further, since when phenylisocrotonic acid is heated, a naphthalene derivative, namely, *a*-naphthol, results, it is clear that the second nucleus is formed by the elimination of a molecule of water with closure of the chain of the four carbon atoms of the side-chain of the original acid and two ortho-carbon atoms in the benzene nucleus :



That there are two condensed benzene nuclei is also deduced from the fact that oxidation of α-nitronaphthalene gives nitrophthalic acid, the benzene nucleus containing the nitro-group being preserved and the other destroyed. If, however, the nitro-group is first reduced to an amino-group, oxidation results in the destruction of the nucleus containing the amino-group and in the preservation of the other, phthalic acid, which undoubtedly contains a benzene nucleus, being formed. That the linkings between carbon and carbon are different in the two nuclei is shown by the addition of four hydrogen atoms to one of the nuclei, which probably has true double linkings, while the other nucleus would seem to have a true benzenic character with centric linkings (Bamberger); further, the addition of ozone proves with certainty the presence of olefinic double linkings (E. Molinari, 1907):

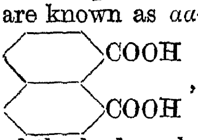


With nitric acid, naphthalene gives a nitro-derivative, and with sulphuric acid, various sulphonic acids. The hydroxy-derivatives resemble phenols and the amino-derivatives are capable of diazotisation.

Hydronaphthalene is readily formed by the addition of nascent hydrogen and behaves likes hydrophenol, *i.e.* like an unsaturated hydrocarbon of the aliphatic series.

The isomerides of the substitution products of naphthalene are more numerous than in the case of benzene. Thus, there are two isomeric mono-substituted derivatives, the α-compound with the substituent in the 1-, 4-, 5-, or 8-position, and the β-compound with the substituent in the 2-, 3-, 6-, or 7-position. The isomeric disubstituted compounds with two similar substituents are ten in number, while with two different substituting groups fourteen isomerides are possible, and, in some cases, all known.

Compounds with substituents in the 1- and 8- or the 4- and 5-positions are known as *αα*- or *peri*-compounds, *e.g.* **Perinaphthalenedicarboxylic Acid**,



, which readily forms an anhydride owing to the proximity of the hydroxyls.

The number of isomerides being so large, it is sometimes difficult to determine the constitution of any derivative. To this end the oxidation products are often studied, the formation of phthalic acid indicating that all the substituents are in the one benzene nucleus destroyed by the oxidation, while the formation of a substituted phthalic acid indicates the opposite to be the case.

NITRONAPHTHALENES, $C_{10}H_7 \cdot NO_2$. Of the two isomerides, the β is of no industrial importance.

α-NITRONAPHTHALENE is obtained on the large scale by nitrating naphthalene (10 parts) with a mixture of 8 parts of nitric acid (sp. gr. 1·49) and 10 parts of sulphuric acid (sp. gr. 1·84), the temperature being kept at 70° for six hours. The supernatant acid is decanted off in the hot and the fused nitronaphthalene washed several times with hot water and then granulated by pouring slowly into cold water with vigorous agitation.

It forms a yellow crystalline mass which melts at 59°, boils at 304°, and in the molten condition has the sp. gr. 1·223; it is insoluble in water but dissolves readily in benzene, ether, carbon disulphide, or hot alcohol.

The crude commercial product costs 64*s.* to 76*s.* per quintal and the pure crystals 96*s.*

It is used in the manufacture of dyestuffs, especially for making α-naphthylamine and thence various azo-derivatives or naphthol derivatives. It is also employed in the

treatment of oils. When it is stored alone, there is no greater danger than in the storage of oil. When used in mixtures not excessively hot, it presents no special danger.

With reducing agents, α-nitronaphthalene gives α-**NAPHTHYLAMINE**, $C_{10}H_7 \cdot NH_2$, and this, by way of the diazo-compound, yields α-naphthol, identical with that obtained from phenylisocrotonic acid. α-Naphthylamine can also be obtained from α-naphthol by means of ammonia and calcium chloride, or ammonia and ammonium sulphite. Industrially it is obtained by the various processes mentioned above for aniline: usually 60 parts of dry α-nitronaphthalene are added gradually to a hot mixture of 80 parts of iron turnings, 4 parts of hydrochloric acid, and a little water, the whole being mixed and kept at 70° for 6 to 8 hours; slaked lime (about 5 parts) is next added until the reaction becomes alkaline, the naphthylamine being distilled from retorts and condensed at 60°, and subsequently purified by rectification. It consists of pleasant-smelling, white crystals, melting at 50°, readily subliming and boiling at 300°. With oxidising agents it gives red or blue colorations. The isomeric β-**NAPHTHYLAMINE** is obtained by heating 10 parts of β-naphthol with 4 parts of caustic soda and 4 parts of ammonium chloride in an autoclave at 160° for 60 to 70 hours; the unchanged naphthol is removed by means of sodium hydroxide solution and the β-naphthylamine extracted from the residue by hydrochloric acid. The preparation with ammonium sulphite (*see above*) gives a better yield owing to the formation of the sulphuric ether of β-naphthol, which reacts more readily with ammonia. It forms shining, odourless scales which melt at 112°, boil at 294°, and are not coloured by oxidising agents. The separation of α- from β-naphthylamine is effected by solvents, such as xylene, chlorobenzene, &c., which dissolve both isomerides in the hot and deposit almost all of the α-compound in the cold.

The commercial α-derivative costs about £8 per quintal and the β-compound three times as much. Both are used for making azo-dyestuffs.

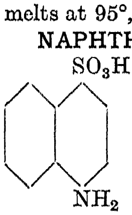
The **NAPHTHALENESULPHONIC ACIDS** are obtained from naphthalene and concentrated sulphuric acid. They form deliquescent crystals and when fused with KOH give the naphthols; the α-sulphonic acid in presence of sulphuric acid at 160° is converted into the β-acid.

α- and β-**NAPHTHOLS**, $C_{10}H_7 \cdot OH$, are found in coal-tar, and may be prepared from the sulphonic acids or amines (*see above*). They form shining scales with a phenolic odour, and dissolve slightly in hot water and more readily in alcohol or ether. α-Naphthol melts at 95° and boils at 282°; β-naphthol melts at 122° and boils at 288°. Their hydroxyl groups are more readily substituted than those of the phenols. With ferric chloride, aqueous α-naphthol gives a violet precipitate, while β-naphthol gives a green coloration and precipitates **Dinaphthol**, $C_{10}H_6 \begin{smallmatrix} \diagup OH \\ \diagdown C_{10}H_6 \cdot OH \end{smallmatrix}$.

The two naphthols give *ethers, e.g.* **Neroline**, $C_{10}H_7 \cdot O \cdot C_2H_5$, which has a fruity odour.

Betol or **Naphthosalol** (the salicylic ester of β-naphthol), $C_{10}H_7 \cdot O \cdot CO \cdot C_6H_4 \cdot OH$, melts at 95°, and is used in medicine under the name of salol.

NAPHTHIONIC ACID (**1-Naphthylamine-4-sulphonic Acid**), $C_{10}H_6(NH_2)(SO_3H)$, or

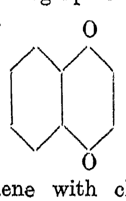


, is formed by sulphonating α-naphthylamine, and is used for preparing Congo red and other dyes. The solutions of its salts have an intense reddish blue fluorescence.

Of the α- and β-naphthylaminesulphonic acids, 13 isomerides are known.

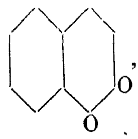
Eikonogen, used as a photographic developer, is the sodium salt of α_1-**Amino**-β-**naphthol**-β_3-**sulphonic Acid.**

α-**NAPHTHAQUINONE**,



, is obtained in yellow crystals melting at 125° by oxidising naphthalene with chromic acid in boiling acetic acid solution. From its constitution those of other substitution products of naphthalene can be

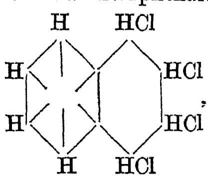
deduced, since when the substituent groups are in the para-position, oxidation always leads ultimately to α-naphthaquinone. It is volatile in steam.

β-NAPHTHAQUINONE, $C_{10}H_6O_2$ or , is formed by the oxidation of 1 : 2-aminonaphthol, and crystallises in reddish yellow leaflets blackening at 115° to 120°.

The following compounds are also known: **Oxy-** and **Dioxynaphthaquinones** (*naphthazarin black*); α- and β-**Methylnaphthalenes**, $C_{10}H_7 \cdot CH_3$; **Naphthoic Acids**, $C_{10}H_7 \cdot CO_2H$; **Hydroxynaphthoic Acids**, $C_{10}H_6(OH)(CO_2H)$; **Naphthalic Acid**, $C_{10}H_6(CO_2H)_2$; **Dinaphthyl**, $C_{10}H_7 \cdot C_{10}H_7$; **Acenaphthene**, $C_{10}H_6\left\langle\begin{array}{l}CH_2\\ | \\ CH_2\end{array}\right.$, in which the unions with the ethylene group are in the α_1- and α_4-positions (found in tar, colourless, melting at 85°, boiling at 277°, and giving naphthalic acid on oxidation).

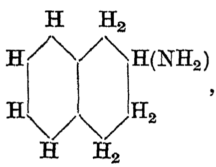
ADDITION PRODUCTS OF NAPHTHALENE

Naphthalene gives additive products more readily than benzene does, those containing four atoms of chlorine or hydrogen being well known. It has been shown that this addition occurs in only one of the nuclei, and similar behaviour is shown on oxidation. Chlorine reacts with naphthalene at the ordinary temperature and forms **Naphthalene Tetrachloride**,

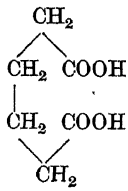


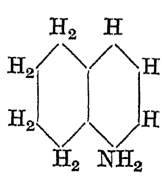
, which forms colourless crystals melting at 181° and gives phthalic acid on oxidation, and **Dichloronaphthalene**, $C_{10}H_6Cl_2$, when treated with alcoholic potash.

When β-naphthylamine is reduced (Na + amyl alcohol), four hydrogen atoms are added to the nucleus containing the amino-group, giving **Tetrahydronaphthylamine**,

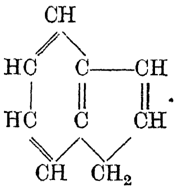


, which behaves exactly like an aliphatic amine and does not form diazo-compounds; it is oxidised by permanganate, giving **o-Carboxyhydrocinnamic Acid**, $C_6H_4\left\langle\begin{array}{l}CH_2 \cdot CH_2 \cdot CO_2H\\ CO_2H\end{array}\right.$. α-Naphthylamine also gives a tetrahydro-derivative, which behaves, however, as an aromatic amine and can be diazotised; on oxidation it gives **Adipic Acid**,

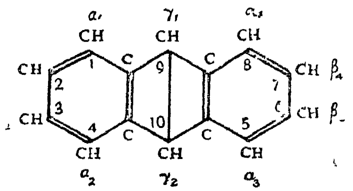


, which shows that the four hydrogen atoms are added to the benzene nucleus which does not contain the amino-group: .

INDENE, C_9H_8, may be regarded as formed by the condensation of a benzene group

with a pentamethylene group :  . It is a yellow oil boiling at 180°, and is found in coal-tar and in crude pseudocumene ; it has an odour of naphthalene and gives phthalic acid on oxidation and **Indrene**, C_9H_{10}, on reduction.

6. ANTHRACENE GROUP

ANTHRACENE, $C_{14}H_{10}$, or  , is found in coal-tar to the extent of 0·25 to 0·45 per cent. The crude anthracene oil which passes over at a high temperature (above 270°) in the distillation of tar is subjected to a further rectification which yields a 50 per cent. anthracene. This is purified by distillation from iron retorts with potassium carbonate, which holds back the large amount of **Carbazole**, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!NH$, as the non-volatile potassium compound, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!NK$. The distillate then contains only anthracene and phenanthrene, the latter being removed by dissolving it in carbon disulphide or a mixture of this solvent with concentrated sulphuric acid (Ger. Pat. 164,508 and Fr. Pat. 349,337). The residual anthracene is purified by crystallisation from crude benzene (*see* Treatment of Tar described on p. 526 *et seq.*), and by sublimation with superheated steam.

The proposal has also been made to purify crude anthracene (containing, say, 46 per cent. of anthracene and 13 per cent. of carbazole) with hot naphtha and sulphuric acid, which convert all the basic substances into salts and dissolve them, the anthracene being afterwards separated by decantation. Evaporation of the naphtha gives anthracene of about 84 per cent. strength and this gives a product of 95 per cent. purity on crystallisation from benzene.

It forms shining, colourless scales with a blue fluorescence, and melts at 216·5° and boils at 351° ; it dissolves slightly in ether or alcohol, but is readily soluble in hot benzene. Sunlight gradually converts it into the polymeric *para*-**Anthracene** $(C_{14}H_{10})_2$. With picric acid it forms a molecular condensation product, $C_{14}H_{10},C_6H_2(NO_2)_3OH$, melting at 138°. By reducing agents, anthracene is transformed into **Hydroanthracene**, $C_6H_4<\begin{matrix} CH_2 \\ CH_2 \end{matrix}>C_6H_4$, which melts at 107° and is readily soluble in alcohol.

It is used for the manufacture of anthraquinone and alizarin.

Crude anthracene oil (green grease) is sold at 11*s.* to 12*s.* 6*d.* per quintal, crude 20 per cent. anthracene at 1*s.* 6*d.* per kilo and the purified product at 6*s.* to 8*s.* per kilo.

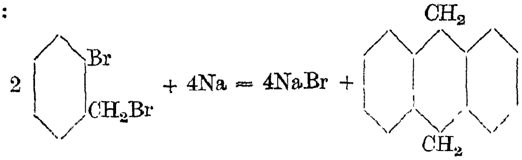
Its constitution is deduced from its various syntheses. Anschütz obtained it from tetrabromoethane and benzene in presence of $AlCl_3$:

$$2C_6H_6 + \begin{matrix} CHBr_2 \\ | \\ CHBr_2 \end{matrix} = 4HBr + C_6H_4\Big\langle \begin{matrix} CH \\ | \\ CH \end{matrix} \Big\rangle C_6H_4.$$

It is formed also when o-tolyl phenyl ketone is heated with zinc dust:

$$C_6H_4\left<\begin{matrix}CH_3\\ \\CO\end{matrix}\right>C_6H_5 = H_2O + C_6H_4\left<\begin{matrix}CH\\|\\CH\end{matrix}\right>C_6H_4;$$

this synthesis establishes the ortho-position of the connections between the two nuclei and also the presence of the $CH\cdot CH$ group. Confirmatory evidence is obtained from the following synthesis:



o-Bromobenzyl bromide   Dihydroanthracene

which, on oxidation, loses 2H and gives anthracene.

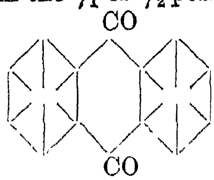
Phthalic anhydride, when heated with benzene and $AlCl_3$, gives o-benzoylbenzoic acid, from which PCl_5 eliminates water with formation of anthraquinone, the latter giving anthracene when reduced with zinc dust in the hot:

$$C_6H_6 + C_6H_4\left<\begin{matrix}CO\\ \\CO\end{matrix}\right>O = C_6H_4\left<\begin{matrix}CO\cdot C_6H_5\\ \\COOH\end{matrix}\right. \longrightarrow H_2O + C_6H_4\left<\begin{matrix}CO\\ \\CO\end{matrix}\right>C_6H_4 \longrightarrow \text{anthracene.}$$

Centric linkings do not seem to be present in the nuclei of anthracene, which readily combine with ozone (E. Molinari, 1907), this property being characteristic of olefine double linkings (*see* p. 88).

SUBSTITUTION PRODUCTS OF ANTHRACENE

The possible isomerides are here very numerous, but only few of them have yet been prepared. Three monosubstituted isomerides are possible, as is seen from the constitutional formula (*see above*). The constitution of the isomerides is ascertained from a study of the oxidation products and of the methods of synthesis. When the substituents are in the γ_1 or γ_2 position, oxidation gives anthraquinone.[1]

ANTHRAQUINONE, $C_{14}H_8O_2$, or  , is obtained very easily by oxidising anthracene with dichromate and dilute sulphuric acid in

[1] Of the many Derivatives of Anthracene, the following may be mentioned: *anthracenecarboxylic acids* (α, β, and γ); *chlorobromoanthracenes*, which contain the halogens in the γ-positions, as they form anthraquinone on oxidation; *nitro-* and *dinitro-anthracenes* (γ); *β-anthramine*, $C_{14}H_9\cdot NH_2$, obtained from β-anthrol and NH_3; *anthrols* (α and β), $C_6H_4\left<\begin{matrix}CH\\|\\CH\end{matrix}\right>C_6H_3\cdot OH$; *anthrone*, $C_6H_4\left<\begin{matrix}CH_2\\ \\CO\end{matrix}\right>C_6H_4$; *$\gamma$-anthranol*, $C_6H_4\left<\begin{matrix}CH\\|\\C(OH)\end{matrix}\right>C_6H_4$; *$\gamma$-hydroanthranol*, $C_6H_4\left<\begin{matrix}CH_2\\ \\CH(OH)\end{matrix}\right>C_6H_4$; the *anthrahydroquinones*, $C_6H_4\left<\begin{matrix}C(OH)\\|\\C(OH)\end{matrix}\right>C_6H_4$ (three isomerides: *chrysazol*, *rufol*, and *flavol*); *anthracenesulphonic* and *disulphonic acids*; *anthraquinonesulphonic acids*; *hydroxyanthraquinones*, $C_{14}H_7O_2\cdot OH$; *quinizarin* ($\alpha_1 : \alpha_2$-dihydroxyanthraquinone); *purpuroxanthin* ($\alpha_1 : \beta_2$-dihydroxyanthraquinone); $C_6H_4(CO_2)\cdot C_6H(OH)_3$ ($\alpha : \beta : \alpha_1$) is *purpurin* (the isomeric *flavopurpurin*, *anthrapurpurin*, *anthragallol*, &c., are also known); $OH\cdot C_6H_3\ CO_2\ C_6H_3\ OH$ (*anthraflavinic* and *isoanthraflavinic acids*, with which correspond *anthrarufin*, *chrysazin*, &c.); *tetrahydroxyanthraquinones* (*rufiopin*, *anthrachrysone*, *quinalizarin*); *hexahydroxyanthraquinones* (*rufigallic acid*, &c.); *methyl-* and *dimethyl-anthracenes*, $C_{14}H_9\cdot CH_3$ and $C_{14}H_8(CH_3)_2$; *phenylanthracene*, $C_{14}H_9\cdot C_6H_5$; *alkylanthrahydrides*, $C_6H_4\left<\begin{matrix}CH_2\\ \\CHR\end{matrix}\right>C_6H_4$; *phenylanthranol* (*phthalidine*), $C_6H_4\left<\begin{matrix}C(C_6H_5)\\|\\C(OH)\end{matrix}\right>C_6H_4$; *phenylhydroxyanthranol* (*phthalideine*), $C_6H_4\left<\begin{matrix}C(C_6H_5)(OH)\\ \\CO\end{matrix}\right>C_6H_4$; *anthracenecarboxylic acids* (α, β, γ), $C_{14}H_9\cdot CO_2H$; *alkylhydroanthranols*, $C_6H_4\left<\begin{matrix}CH_2\\ \\CR(OH)\end{matrix}\right>C_6H_4$, &c.

the hot, or, better, with nitric acid, which does not give nitro-derivatives. It can also be obtained from phthalic anhydride and benzene in presence of $AlCl_3$ (*see above*) or by electrolysing anthracene in 20 per cent. sulphuric acid in presence of cerium, chromium, or manganese salts (Ger. Pat. 152,063, and Perkin, 1904).

It can be purified by crystallisation from nitrobenzene or aniline, which dissolve it in the hot but not in the cold. It gives two isomeric monosubstituted derivatives.

It forms yellowish needles melting at 274° and boiling at about 360°, and it dissolves in concentrated sulphuric acid, but is precipitated unchanged on dilution. It is very stable, is not easily oxidised and has the character of a diketone rather than of a quinone. It is not readily reduced, is only slightly volatile and has no pungent odour. That the two lateral benzene nuclei have centric linkings and not olefinic double bonds is shown by the fact that, unlike anthracene (*see above*), anthraquinone does not fix ozone.

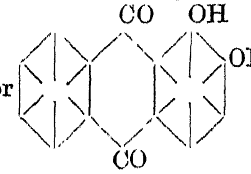
When fused with potash, it gives benzoic acid and, when heated with zinc dust and NaOH, Hydroxyanthranol, $C_6H_4<\genfrac{}{}{0pt}{}{CH(OH)}{—CO—}>C_6H_4$, which has a blood-red colour in alkaline solution and is oxidised to anthraquinone in the air. Reduction of anthraquinone with Sn and HCl gives Anthranol,

$$C_6H_4\left\langle\begin{array}{c}C(OH)\\ |\\ C(OH)\end{array}\right\rangle C_6H_4,$$ which is a weak phenol.

More energetic reduction, such as distillation over zinc dust, yields anthracene. The Bohn-Schmidt reaction permits of the introduction of sulphonic or nitro-groups into the non-substituted or the substituted nucleus of anthraquinone derivatives, according as the reaction occurs in presence or in absence of boric acid. α- or β-Nitroderivatives can also be obtained, at will, by means of the same reaction (Ger. Pat. 163,042 of 1905), which is facilitated by the presence of mercury salts.

Commercial anthraquinone costs about 6*s*. per kilo, and the sublimed chemically pure product 28*s*.

The most important derivative of anthraquinone is the 1 : 2-dihydroxy-compound or alizarin.

ALIZARIN (Dihydroxyanthraquinone), $C_{14}H_8O_4$, or ,

was at one time obtained exclusively from madder roots (*Rubia tinctorum*), from which **Ruberythric Acid** (a glucoside of the formula $C_{26}H_{28}O_{14}$) is extracted, this is separated into glucose and alizarin by boiling with dilute sulphuric acid. It is a very beautiful red colouring-matter and was known to the ancients. Since 1870,[1] following Gräbe and Liebermann's synthesis (1869), it has been prepared only artificially in the following manner : anthracene is converted by oxidation with H_2SO_4 and $Na_2Cr_2O_7$ into crude anthracene.

This is then heated at 100° with concentrated sulphuric acid, which leaves the anthraquinone unaltered, while it converts the impurities into sulphonic acids soluble in water. The anthraquinone is then filtered and washed and heated at 160° with fuming sulphuric acid (containing 50 per cent. of free SO_3), which converts it largely into the monosulphonic acid. The latter is dissolved in water and filtered to separate it from unaltered anthraquinone ; neutralisation of the solution with caustic soda results in the deposition of the sodium salt, which is only slightly soluble in cold water. One hundred parts of this salt are mixed with 25 parts of caustic soda and 12 to 14 parts of potassium chlorate, which facilitates

[1] In 1868 France produced and exported madder to the value of £1,720,000 and £1,240,000 respectively. The exportation fell to £800,000 in 1871 and to £160,000 in 1876, the production then ceasing entirely.

the reaction ; the mixture is dissolved in the smallest possible amount of water and the liquid heated at 180° for 2 days in an autoclave fitted with a stirrer. The sulphonic group is thus replaced by hydroxyl (or ONa), and at the same time a second OH group is formed by the action of the chlorate :

$$C_6H_4{<}^{CO}_{CO}{>}C_6H_3\cdot SO_3Na + 3NaOH + O = Na_2SO_3 + 2H_2O + C_6H_4{<}^{CO}_{CO}{>}C_6H_2(ONa)_2.$$

Sodium anthraquinone-monosulphonate

The fused mass is run into water and acidified with sulphuric acid, the colouring-matter (alizarin) being thus liberated.

According to Fr. Pat. 333,144, if fuming sulphuric acid acts on anthraquinone in presence of mercury, there is no partial formation of the m-sulphonic compound, the sulpho-group entering exclusively the ortho-position to the ketonic group.

Alizarin may also be prepared (Ger. Pat. 186,526) without sulphonation by treating, say, 300 kilos of a mixture of NaOH and KOH with 30 kilos of $NaClO_3$ (or Na_2O_2, BaO_2, PbO_2, &c.) dissolved in 100 litres of water, 100 kilos of anthraquinone being then added and the liquid heated at 200° in an oil-bath until the oxidising agent disappears. After this, the mass is poured into water through which air is then passed ; the alizarin is precipitated with milk of lime, the precipitate being filtered off and decomposed with HCl and the alizarin purified from anthraquinone residues by means of caustic soda. This method yields a purer product than other processes.

Alizarin has been prepared recently by passing an electric current through a mixture of anthraquinone and fused potash.

Alizarin sublimes in fine, orange-red needles, melts at 289°, and is almost insoluble in water and slightly soluble in alcohol ; owing to its phenolic groups it dissolves in alkali and also forms a diacetyl-derivative. When distilled with zinc dust it forms anthracene.

With metallic oxides it forms insoluble lakes of various colours, and on this is based its use in dyeing. With ferric oxide it gives a bluish black colour and with lime a blue lake ; the lakes of tin and aluminium are red (Turkey red).

The constitution of alizarin is shown also by its synthesis from phthalic anhydride and catechol at 150° in presence of sulphuric acid :

$$C_6H_4{<}^{CO}_{CO}{>}O + C_6H_4{<}^{OH\,(1)}_{OH\,(2)} = H_2O + C_6H_4{<}^{CO}_{CO}{>}C_6H_2{<}^{OH}_{OH}.$$

Derivatives of anthraquinone and of hydroxyanthraquinone, especially the amino-derivatives, form *colouring-matters* only when the two hydroxy-groups are in the ortho-position to one another.

PHENANTHRENE, $C_{14}H_{10}$, or $\begin{array}{c}C_6H_4\cdot CH\\ |\qquad\;\;\|\\ C_6H_4\cdot CH\end{array}$, is an isomeride of anthracene, with which it occurs in tar. When pure, it forms shining, colourless scales, soluble in ether, less so in alcohol (with blue fluorescence) and only slightly soluble in water ; it melts at 99° and boils at 340°. The separation of phenanthrene from anthracene is described above (*see* Anthracene). Synthetically it is obtained by condensing 1 mol. of o-nitrobenzaldehyde (or its higher homologues) with 1 mol. of sodium phenylacetate in presence of acetic anhydride :

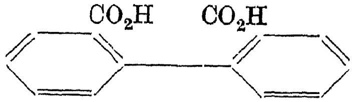
$$C_6H_5\cdot CH_2\cdot CO_2Na + NO_2\cdot C_6H_4\cdot CHO = H_2O + \begin{array}{r}NO_2\cdot C_6H_4\cdot CH\\ \|\;\;\\ C_6H_5\cdot C\cdot CO_2Na\end{array}$$

Sodium α-phenyl-o-nitrocinnamate

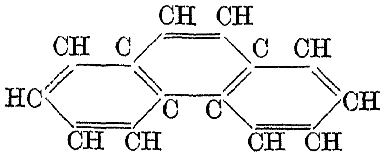
Reduction and diazotisation eliminate the NO_2, treatment with powdered

copper then gives β-Phenanthrenecarboxylic Acid, $\begin{array}{l} C_6H_4\text{—}CH \\ | \qquad \| \\ C_6H_4\text{—}C\cdot CO_2H \end{array}$, from which CO_2 is eliminated in the ordinary way with formation of phenanthrene.

When oxidised with chromic acid, it gives first Phenanthraquinone, $\begin{array}{l} C_6H_4\cdot CO \\ | \qquad | \\ C_6H_4\cdot CO \end{array}$ (yellow crystals, m.pt. 200°), and then Diphenic Acid, $C_{14}H_{10}O_4$, or

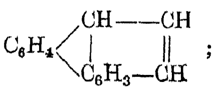


The constitution of phenanthrene is established by its syntheses and by its oxidation products. The double linking between the two methinic carbon atoms is not shown by the ordinary reaction with permanganate (Baeyer) (*see* p. 88), but is made evident by the reaction with ozone (E. Molinari, 1907; *see* p. 88). The constitutional formula of phenanthrene may be represented thus:



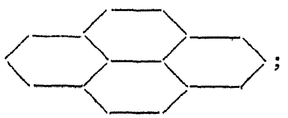
and it may, therefore, be regarded as formed by the condensation of three benzene nuclei.

OTHER CONDENSED NUCLEI OF LESS IMPORTANCE, found in the portions of petroleum and tar distilling above 360°, are as follow:



;

Fluoranthrene, $C_{15}H_{10}$


;

Pyrene, $C_{16}H_{10}$

$$\begin{array}{l} C_6H_4\text{—}CH \\ | \qquad\ \ \| \\ C_{10}H_6\text{—}CH \end{array};$$

Chrysene, $C_{18}H_{12}$

$$\begin{array}{l} C_{10}H_6\text{—}CH \\ | \qquad\quad \| \\ C_{10}H_6\text{—}CH \end{array};$$

Picene, $C_{22}H_{14}$

$$\begin{array}{l} \qquad\quad C_6H_4\text{—}CH \\ CH_3\diagdown \ | \qquad \| \\ \qquad\quad C_6H_2\text{—}CH \\ C_3H_7\diagup \end{array}.$$

Retene, $C_{18}H_{18}$

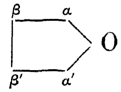
Retene has m.pt. 98° and b.pt. 394°; **Chrysene**, m.pt. 250°, b.pt. 448°; **Picene**, m.pt. 364°; **Fluoranthrene**, m.pt. 110° and b.pt. 250° (60 mm.); **Pyrene**, m.pt. 148°, b.pt. 260° (60 mm.).

Q. HETEROCYCLIC COMPOUNDS

These are substances containing at least one nucleus, the atoms forming the ring being of more than one kind, *i.e.* they are not all carbon atoms as in the *homocyclic compounds* as yet studied, one or more of these carbon atoms being replaced by nitrogen, oxygen, sulphur, &c. One of the simplest of these heterocyclic compounds is furfuran.

1. **FURFURAN** (Furan), C_4H_4O, is a colourless liquid which is insoluble in water, smells like chloroform, boils at 32°, and is found among the first products of the distillation of pine-tar. With metallic sodium it does not give hydrogen, so that the oxygen is not present as OH; nor is it in the form of carbonyl (CO), since furan does not react with phenylhydrazine or hydroxylamine. It can be converted into cœrulinic aldehyde, while, under suitable

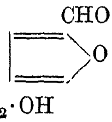
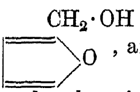
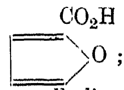
conditions, succindialdehyde loses H_2O giving furan. These reactions indicate its constitution :

$$\begin{array}{l} CH_2\cdot CHO \\ | \\ CH_2\cdot CHO \end{array} = H_2O + \begin{array}{l} CH : CH \\ | \\ CH : CH \end{array}\!\!\!>O \quad ($$  $)$

Succindialdehyde — Furan

A shaving of pinewood moistened with HCl gives a green coloration with furan. The latter reacts with HCl forming a white mass.

FURFURAL (α-Furol, Furfuraldehyde), $C_5H_4O_2$, is obtained readily and abundantly by the action of sulphuric acid on pentoses, pentosans, and woody substances (*see* p. 429) ; it is found in fusel oil and in clove oil. It is a colourless oil of aromatic odour, turning brown in the air and boiling at 162° ; it is soluble in alcohol and, to a less extent, in water.

Its aldehydic properties justify the constitution  . With alcoholic potash it gives a corresponding Furfuryl Alcohol,  , and Pyromucic Acid,  ; the latter melts at 132°, sublimes readily, dissolves in hot water, decolorises alkaline permanganate and combines with 4 atoms of bromine, the presence of two true olefinic double linkings being thus confirmed. If heated in a sealed tube at 275° it gives furfuran and CO_2. With aniline and HCl, or with aniline acetate paper, it gives a characteristic intense red coloration (*see* p. 430).

2. **THIOPHENE**, C_4H_4S, occurs in tar and always accompanies benzene, on account of their similarity in boiling-point (84°) and other properties. For the preparation of benzene free from thiophene, *see* p. 533.

Thiophene is produced on a large scale, but in small yield, by passing acetylene or ethylene through boiling sulphur, or by passing illuminating gas over red-hot pyrites. W. Steinkopf (1911) obtains an increased yield by passing a current of acetylene over pyrites contained in a revolving iron drum and heated to 300° in a furnace, the exhausted pyrites being continually discharged and fresh pyrites introduced. The condensed liquid product contains 40 per cent. of thiophene, which can be extracted by fractional distillation.

One of the syntheses of thiophene consists in the distillation of succinic acid in presence of phosphorus sulphide, hydrogen and hydrogen sulphide being evolved ; this synthesis confirms the constitution :

$$\begin{array}{l} H_2C\cdot CO_2H \\ \quad | \\ H_2C\cdot CO_2H \end{array} \longrightarrow \begin{array}{l} \overset{\beta}{HC} = \overset{\alpha}{CH} \\ \ \ | \\ \underset{\beta^1}{HC} = \underset{\alpha^1}{CH} \end{array}\!\!\!>S \quad \text{(Thiophene).}$$

Thiophene is a colourless and almost odourless, refractive liquid, boiling at 84°, and having the sp. gr. 1·062 at 23°. The presence of the double linkings is confirmed by the quantitative addition of ozone.

Pure thiophene, prepared synthetically, costs £18 per kilo.

Dimethylthiophene (*thioxene*), $\begin{array}{l} CH : C(CH_3) \\ | \\ CH : C(CH_3) \end{array}\!\!\!>S$, is obtained by the interaction of the enolic form of acetonylacetone and phosphorus pentasulphide, and 1 : 4-diketones in general yield higher homologues of thiophene, which, when oxidised, give carboxyl groups in place of the side-chains.

Thiophene compounds, such as halogen and nitro-derivatives, sulphonic acids, &c., behave very similarly to those of benzene.

With isatin and concentrated sulphuric acid, thiophene gives a blue coloration (*indophenin*, $C_{12}H_7\cdot NOS$).

3. **PYRROLE**, C_4H_5N, is found in small quantity in tar and in larger quantity in Dippel animal oil (*bone oil*), especially in the fraction distilling at about 130°, which is freed from pyridine bases by saponifying with soda and washing with dilute sulphuric

acid. It is purified by converting into the potassium derivative, C_4H_4NK (by the action of potassium), which is washed with ether, in which it is insoluble, and then treated with water, the pyrrole being thus liberated.

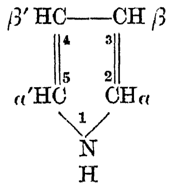
After fractional distillation, it is obtained as a light, colourless oil, boiling at 131°, and possessing a faint odour of chloroform. It readily turns brown and polymerises under the action of light. With isatin and sulphuric acid it gives the blue indophenin reaction (*see above*).

A *reaction characteristic of the pyrroles* is the red coloration they give with a pine shaving moistened with HCl.

The hydrogen of the iminic group is replaceable by metals, acetyl, and alkyl groups.

Pyrrole now forms the basis of a number of important compounds, which are obtained by various syntheses investigated by Ciamician and his collaborators during the past quarter of a century.

The constitutional formula of pyrrole is as follows:



this being deduced from a number of reactions and syntheses, *e.g.* the formation of pyrrole by the action of ammonia on γ-diketones or on succinic aldehyde, with intermediate formation of diammonaldehyde:

$$\begin{array}{l} CH_2\cdot CHO \\ | \\ CH_2\cdot CHO \end{array} + NH_3 = 2H_2O + \begin{array}{l} CH:CH \\ | \\ CH:CH \end{array}\!\!>NH.$$

This pyridine nucleus occurs frequently in nature, in combination with other groups in alkaloids (nicotine, &c.), in the colouring-matter of the blood and of chlorophyll, &c.

When boiled with hydroxylamine, pyrrole gives **Succindialdoxime**, $\begin{array}{l} CH_2\cdot CH:N\cdot OH \\ | \\ CH_2\cdot CH:N\cdot OH \end{array}$,

which, with nitrous acid, gives succinic aldehyde, $\begin{array}{l} CH_2\cdot CHO \\ | \\ CH_2\cdot CHO \end{array}$.

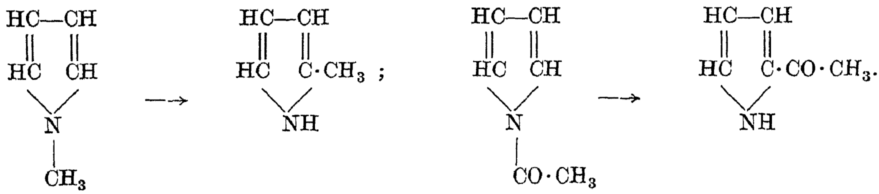
Pyrrole is formed by the distillation of succinimide, $\begin{array}{l} CH_2\cdot CO \\ | \\ CH_2\cdot CO \end{array}\!\!>NH$, with sodium or zinc dust, while the oxidation of pyrrole with chromic acid gives maleimide, $\begin{array}{l} CH\cdot CO \\ \| \\ CH\cdot CO \end{array}\!\!>NH$.

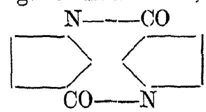
Pyrrole is changed by acids; with HCl in the hot, it polymerises and condenses to a red mass (*pyrrole red*). It has a faint acid character, but gives a hydrochloride, $(C_4H_5N)_3$, HCl, only in ethereal solution.

With the halogens it gives not additive products but only, like benzene, substituted derivatives. **Tetraiodopyrrole** (*iodol*) is obtained from pyrrole by the action of an alcoholic, alkaline solution of iodine; it is an efficient antiseptic and is used instead of iodoform, being without the unpleasant odour of the latter. It melts at 190°, and is colourless when freshly prepared, but it gradually turns brown and deposits iodine.

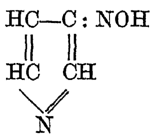
With nitric and sulphuric acids, pyrrole resinifies; the nitro-derivatives, which contain the *isonitro*-group, NOOH, are prepared indirectly (*e.g.* with alkyl nitrate).

Pyrrole is analogous in many of its properties with the substituted phenols and anilines; thus, a methyl- or acetyl-group united to the nitrogen (N-derivatives) is displaced, on heating, to a carbon atom (C-derivatives):

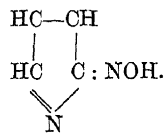


Potassium pyrrolate, C_4H_4NK, and CO_2 give pyrrolecarboxylic acid, $C_4H_3(CO_2H)\cdot NH$ (m.pt. 102°); this loses CO_2 and gives pyrrole again when heated, while it loses water and forms a dimolecular anhydride, **Pyrocoll**, , when treated with acetic anhydride.

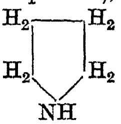
Like the substituted phenols, the C-alkylpyrroles give pyrrolecarboxylic acids by simple fusion with potash. In analogy with the formation of nitrosophenols from phenols, pyrrole, with ethyl nitrite in presence of sodium alkoxide, forms **Nitrosopyrrole**, which exists in tautomeric modifications:

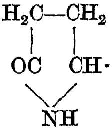


and

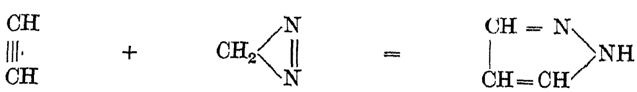


By means of chloroform and sodium alkoxide, another atom of carbon is introduced into the nucleus, a pyridine derivative being formed.

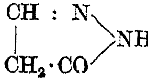
Hydrogenated derivatives of pyrrole are formed more easily than those of benzene, and, like the latter, do not show purely aromatic properties. When pyrrole is reduced by means of zinc and hot acetic or cold hydrochloric acid, it yields **Dihydropyrrole** (or *pyrroline*, m.pt. 91°), which, with HI and P, gives **Tetrahydropyrrole** (or *pyrrolidine*, b.pt. 87°), ; the latter, together with N-methylpyrroline, are the simplest cyclic alkaloids known and are found in tobacco. Pyrrolidine is found in carrot seeds and a C-methylpyrroline in pepper.

When proteins are decomposed by means of trypsin or hydrochloric acid, the amino-acids formed are accompanied by lævo-rotatory **α-Pyrrolidinecarboxylic Acid.** Among the products formed by the degradation of egg albumin by baryta is **α′-pyrrolidone-α-carboxylic Acid**, , which is also known as *pyroglutamic acid*; it melts at 183°, has a neutral reaction and, when heated, loses CO_2 and H_2O, forming pyrrole.

PYRAZOLE, $C_3H_4N_2$, is a heterocyclic compound with two nitrogen atoms in the ortho-positions. It can, indeed, be obtained by the condensation of 1 mol. of diazomethane with 1 mol. of acetylene:



(**Pyrazole**).

It is very stable, melts at 70°, is a feeble base, and has a neutral reaction in water. The $\alpha'\beta'$-dihydro-compound is known as **Pyrazoline**, $C_3H_6N_2$, and the α′-keto-derivative of this, , as **Pyrazolone**. Condensation of methylphenylhydrazine,

$CH_3\cdot NH\cdot NH\cdot C_6H_5$, with ethyl acetoacetate yields **Dimethylphenylpyrazolone,** $\begin{array}{l} CH_3\cdot C{-}N(CH_3) \\ \quad\| \\ H\cdot C{-}{-}{-}CO \end{array}\!\!>N\cdot C_6H_5$, which bears the name *antipyrine* and is used medicinally owing to its marked antipyretic action on the animal organism; it melts at 113°, dissolves in water and in alcohol, and gives a greenish blue coloration with nitrous acid and a red coloration with ferric chloride.

THIAZOLE, C_3H_3NS, or $\begin{array}{l} NC{=}H \\ | \\ CH{=}CH \end{array}\!\!>S$, may be regarded as thiophene with one CH group replaced by N. It shows analogies with the pyridine bases. Just as benzene may be obtained from aniline, thiazole may be obtained from aminothiazole (*see below*).

AMINOTHIAZOLE, $C_3H_2NS\cdot NH_2$, is obtained by the action of monochloracetaldehyde on pseudo-thiourea:

$$\begin{array}{l} CH_2\cdot Cl \\ | \\ CHO \end{array} + \begin{array}{l} HN \\ \\ HS \end{array}\!\!>C{-}NH_2 = HCl + H_2O + \begin{array}{l} CH{-}N \\ \| \\ CH{-}S \end{array}\!\!>C\cdot NH_2,$$

and is a base analogous to aniline.

IMIDAZOLE or Glyoxaline, $C_3H_4N_2$ or $\begin{array}{l} N{=}CH \\ | \\ HC{=}CH \end{array}\!\!>NH$, melting at 92°, is a strong base with a fishy odour, and is isomeric with pyrazole (*see above*); it is obtained by the action of ammonia on glyoxal in presence of a little formaldehyde. Alloxan (*see* p. 366) may be regarded as a derivative of imidazole.

LYSIDINE, Methyldihydroimidazole or Ethenylethylenediamine, $C_3H_3(CH_3)N_2H_2$, is administered as a solvent for uric acid.

OXAZOLE, C_3H_3NO, or $\begin{array}{l} N{=}CH \\ | \\ HC{=}CH \end{array}\!\!>O$, is also termed Furazole, owing to its analogy with furfuran (*see above*). Its phenyl derivatives are known, as also are those of **Isooxazole,** $\begin{array}{l} HC{=}N \\ | \\ HC{=}CH \end{array}\!\!>O$.

OSOTRIAZOLE, $\begin{array}{l} HC{=}N \\ | \\ HC{=}N \end{array}\!\!>NH$, is faintly acid and also faintly basic in character. It melts at 22°, boils at 204°, and is soluble in water.

TRIAZOLE (or Pyrrodiazole), $\begin{array}{l} N{=}CH \\ | \\ HC{=}N \end{array}\!\!>NH$, melts at 121°, and is extremely soluble in water.

TETRAZOLE, $\begin{array}{l} HC{=}N \\ | \\ N{=}N \end{array}\!\!>NH$, is a weak acid which forms explosive salts; it melts at 155° and is soluble in water.

AZOXAZOLE, $\begin{array}{l} HC{=}N \\ | \\ HC{=}N \end{array}\!\!>O$, is also termed **Furazan.**

4. PYRIDINE AND ITS DERIVATIVES

Pyridine is a heterocyclic nucleus containing five carbon atoms and one nitrogen. It resembles benzene in its behaviour, but it is more stable or more indifferent towards sulphuric, nitric, and chromic acids, permanganate, &c. Oxidation of the homologues with side-chains gives pyridinecarboxylic acids, and the latter, when distilled with lime, give pyridine.

Its hydro-derivatives are readily formed in a similar manner to hydrobenzenes.

Halogen derivatives are obtained more easily by the action of PCl_5 or $SbCl_5$ at a high temperature than by the action of the halogens themselves.

Oxidising agents attack only the side-chains and not the pyridine nucleus. With sulphuric acid, a pyridinesulphonic acid is obtained, and this gives a hydroxyl-derivative of pyridine on fusion with potash, or a nitrile when treated with KCN. There is hence a marked analogy to benzene, although direct nitration of pyridine is not possible unless phenolic or aminic groups are present.

Pyridine and its derivatives are decidedly basic in character (tertiary bases) and form soluble salts with hydrochloric or sulphuric acid and insoluble ones with chromic acid; the double salts with platinum and gold chlorides are slightly soluble. Like tertiary bases, they combine with methyl iodide to form quaternary bases.

From the complex alkaloidal groupings, pyridine compounds are often obtained either by distillation with caustic potash or merely by energetic oxidation.

Coal-tar and Dippel animal oil contain various pyridine compounds which are separated by conversion into salts.

General methods of formation. (*a*) The oxidation of quinoline (*see later*) yields first quinolinic acid (pyridinedicarboxylic acid), $C_5H_3N(CO_2H)_2$, which then loses CO_2, giving pyridine. β-Methylpyridine is obtained by distilling acraldehyde-ammonia; this explains the presence of pyridine products in Dippel oil, acroleïn and ammonia being formed in the dry distillation of non-defatted bones.

An important synthesis is the general one of Hantzsch by which **Ethyl Dihydrocollidinedicarboxylate**, for example, is obtained by heating aldehyde-ammonia with ethyl acetoacetate; other pyridine compounds are obtained from different aldehyde-ammonias and β-ketonic acids:

$$2CH_3\cdot CO\cdot CH_2\cdot CO_2C_2H_5 + CH_3\cdot CHO + NH_3 = C_5N(CH_3)_3H_2(CO_2C_2H_5)_2 + 3H_2O.$$

From the ester thus formed the hydrogen of the NH and CH is eliminated by means of nitrous acid, and the resulting collidinedicarboxylic acid, when treated with potash and distilled with lime, loses the two carboxyls and gives collidine (trimethylpyridine); oxidation of the latter gives pyridinecarboxylic acid and elimination of carboxyl from this in the ordinary way forms pyridine.

When ethylidene chloride is heated with alcoholic ammonia, it yields **Aldehydine**, $C_8H_{11}\cdot N$.

The *constitution of pyridine* corresponds with that of benzene, in which one methinic group, CH, has been replaced by a nitrogen atom. Körner in 1869 proposed the following constitutional formula, which still agrees well with all the general properties of the pyridine compounds:

When pyridine is reduced with alcohol and sodium, it fixes six atoms of hydrogen, giving **Piperidine** or hexahydropyridine, the constitution of which is shown by its synthesis when pentamethylenediamine hydrochloride is rapidly heated:

$$CH_2\begin{cases} CH_2\cdot CH_2\cdot NH_2 \\ CH_2\cdot CH_2\cdot NH_2 \end{cases} = NH_3 + CH_2\begin{cases} CH_2\cdot CH_2 \\ CH_2\cdot CH_2 \end{cases}\!\!NH.$$

When piperidine is heated with sulphuric acid it gives pyridine, and the latter, when strongly heated with hydriodic acid, gives normal pentane. The constitution of pyridine is confirmed by the fact that the isomeric substitution products correspond exactly in number with those derivable theoretically from Korner's formula. There are, indeed, three monosubstituted isomerides (α, β, and γ), and six disubstituted isomerides: $\alpha\alpha'$, $\alpha\beta$, $\alpha\beta'$, $\beta\gamma$, and $\beta\beta'$.

The position of a substituent group is determined by converting it into a carboxyl group with formation of the corresponding acid of known constitution (*see later*). Thus, picolinic acid has the carboxyl in the α-position, nicotinic acid in the β-, and isonicotinic acid in the γ-position.

PYRIDINE, C_5H_5N, is a colourless liquid, boiling at 115° and having the sp. gr. 1·0033 at 0°. It dissolves in water in all proportions and has a slight alkaline reaction (not sensitive to phenolphthalein, slightly to litmus, and more so to methyl orange).

It has an unpleasant odour and is hence used to denature alcohol (*see* p. 152).

It forms a slightly soluble ferrocyanide, by means of which it can be purified. It forms pyridineammonium iodides, *e.g.* C_5H_5N,CH_3I, which with KOH in the hot gives Dihydromethylpyridine, $C_5H_4H_2\cdot NCH_3$, with a characteristic pungent odour.

Metallic sodium polymerises pyridine, forming Dipyridine, $C_{10}H_{10}N_2$ (b.pt. 290°) and γ-Dipyridyl, $C_{10}H_8N_2$ or $NC_5H_4\cdot C_5H_4N$ (m.pt. 114°). With sulphuric acid it gives β-Pyridinesulphonic Acid, $NC_5H_4\cdot SO_3H$.

Pyridine is administered in cases of asthma and has been suggested as a means of purifying synthetic indigo.

Mixed pyridine bases for denaturing cost about 1*s*. 2*d*. per kilo and pure pyridine 8*s*.

Of the homologues of pyridine, the following may be mentioned:

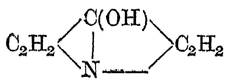
PICOLINE (Methylpyridine), $NC_5H_4\cdot CH_3$, exists as three isomeric liquids similar to pyridine and of disagreeable odour; their boiling-points are: α, 129°; β, 142°; γ, 144°. Besides by general synthetical methods (*see above*), β-picoline is formed by heating strychnine with lime. α-Methylpyridine condenses with aldehydes by means of the methyl group, giving *alkines*: $NC_5H_4\cdot CH_3 + CH_3\cdot CHO = NC_5H_4\cdot CH_2\cdot CH(OH)\cdot CH_3$. This α-*picolylalkine* gives up a molecule of water yielding a pyridine derivative with an unsaturated side-chain, *e.g.*, α-allylpyridine, $NC_5H_4\cdot CH : CH\cdot CH_3$.

These reactions proceed in one stage if zinc chloride is present with the aldehyde.

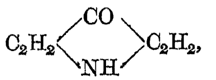
LUTIDINES (Dimethylpyridines), $NC_5H_3(CH_3)_2$; three isomerides are known, with the boiling-points: $\alpha\alpha'$, 143°; $\beta\beta'$, 170°; $\alpha\gamma$, 157°.

COLLIDINES (Trimethylpyridines), $NC_5H_2(CH_3)_3$, are isomeric with propylpyridine. α-Allylpyridine (*see above*) fixes hydrogen (alcohol and sodium), giving the alkaloid CONIINE (inactive racemic), which is α-Propylpiperidine; fractional crystallisation of the tartrate separates the lævo- from the dextro-form, the latter being identical with natural coniine (the poison of hemlock), boiling at 167°. The asymmetric carbon atom causing the activity is the α- one united with the propyl group.

PYRIDONES or HYDROXYPYRIDINES, $NC_5H_4\cdot OH$. The three isomerides are known, their boiling-points being: α, 107°; β, 124°, and γ, 148°. They are obtained by heating the corresponding hydroxypyridinecarboxylic acids with lime. They are phenolic in character and give red or yellow colorations with ferric chloride. α-Hydroxypyridine forms two series of derivatives corresponding with the two tautomeric formulæ:



and



the former giving, for instance, a Methoxypyridine and the latter a Methylpyridone.

PYRIDINEMONOCARBOXYLIC ACIDS, $NC_5H_4\cdot CO_2H$. The three isomerides are as follow: α or Picolinic Acid, m.pt. 135°; β or Nicotinic or Nicotic Acid, m.pt. 231°; γ or isonicotinic acid, m.pt. 309°.

They are formed by oxidation of pyridine derivatives with a side-chain or by elimination

of one carboxyl from the pyridinedicarboxylic acids, that nearer to the nitrogen being the more easily eliminated. Nicotinic acid is obtained on oxidation of nicotine. When boiled with sodium amalgam in a highly alkaline solution, these acids lose nitrogen as NH_3 and give saturated, open-chain, dibasic hydroxy-acids.

When the carboxyl is in the α-position (with the dicarboxylic acids also), an orange coloration is given with $FeSO_4$.

As they are both acid and basic in character, they exhibit analogies with glycocoll (*see* p. 355).

The **PYRIDINEDICARBOXYLIC ACIDS**, $NC_5H_3(CO_2H)_2$, have the following melting-points: $\alpha\alpha'$ or **Dipicolinic Acid**, 226°; $\beta\beta'$ or **Dinicotinic Acid**, 323°; $\alpha\beta$ or **Quinolinic Acid**, 190°; **Isocinchomeronic Acid**, 236°; $\alpha\gamma$ or **Lutidinic Acid**, 235°; $\beta\gamma$ or **Cinchomeronic Acid**, 249°.

Quinolinic acid is formed by the oxidation of quinoline, its constitution being thus established; and since in the hot it loses CO_2 from the α-position, giving nicotinic acid, the constitution of the latter is also fixed.

Pyridinetricarboxylic Acids (obtained by oxidising cinchonine or quinine), as well as **Pentacarboxylic Acids** and **Hydroxypyridinecarboxylic Acids**, are also known.

HYDROPYRIDINES. The **Dihydropyridines** are mentioned above. The *tetrahydropyridines* and their derivatives are known also as *piperideines*, while the *hexahydropyridines* and their derivatives—included in the term *piperidines*—embrace *pipecoline*, $NC_5H_{10}\cdot CH_3$; *lupetidine*, $NC_5H_9(CH_3)_2$; *copellidine*, $NC_5H_8(CH_3)_3$, &c.

PIPERIDINE, NC_5H_{11}, is obtained by heating **Piperine** or *piperylpiperidine*, $C_5H_{10}N\cdot C_{12}H_9O_3$ (m.pt. 129°), which is the alkaloid contained in pepper, and is formed by the condensation of 1 mol. of *piperic* or *piperinic acid*, $C_{12}H_{10}O_4$, or

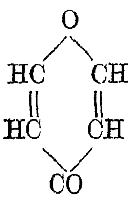
$$CH_2{<}{}^{O}_{O}{>}C_6H_3\cdot CH : CH\cdot CH : CH\cdot CO_2H$$

with 1 mol. of piperidine. For the constitution and syntheses of the latter, *see* p. 624.

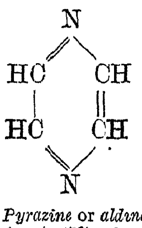
Piperidine boils at 106°, has an odour of pepper, is strongly basic, and is soluble in water or alcohol. With H_2O_2 it gives aminovaleraldehyde.

Piperidine, being a secondary base, forms with $2CH_3I$ an ammonium iodide derivative which, when distilled with silver oxide, gives an unsaturated open-chain, tertiary base; in its turn the latter, with CH_3I, Ag_2O, and distillation, loses trimethylamine and forms **Piperilene**, $CH_2 : CH\cdot CH_2\cdot CH : CH_2$.

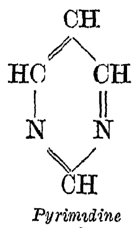
To the group of heterocyclic compounds belong the following, which are of little importance:



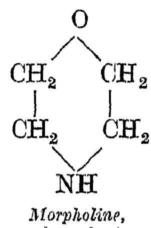
Pyrone or *pyrocomane* (m.pt. 32°); the isomeric α-pyrone is *coumalin*



Pyrazine or *aldine* (m.pt. 47°) is basic and with H gives *piperazine*, $C_4H_{10}N_2$



Pyrimidine or m-diazine (m.pt. 22°)



Morpholine, a base, b.pt. 129°

From these compounds can be derived *coumalinic* or *comanic acid*, $C_5H_3O_2\cdot CO_2H$ (also formed from malic acid); **Meconic Acid**, $C_5HO_2(OH)(CO_2H)_2$, which can be obtained from opium and gives *pyromeconic acid* by elimination of CO_2; **Chelidonic Acid**, $C_5H_2O_2(CO_2H)_2$, which is found in celandine, loses CO_2 giving comanic acid and pyrone.

ALKALOIDS

These are found in various plants and have medicinal and often poisonous properties; some of them, such as caffeine, theobromine, &c., were described on p. 368, and the principal ones having basic characters (*vegetable bases*) will be considered here.

They are almost all lævo-rotatory and have an alkaline reaction and a bitter taste. They are soluble in alcohol and to a less extent in ether, and are usually insoluble in water and in alkali; in acids they dissolve with formation of crystallisable salts. Nearly all alkaloids are precipitated from their solutions by tannin, phosphomolybdic acid, potassium mercury iodide, HgI_2,KI, or aromatic nitro-derivatives (*e.g.* picric acid, &c.), &c.[1] From plants they are extracted with acid solutions and are then liberated with alkali and either distilled in steam or, if they are non-volatile, filtered.

When converted into salts by means of strong acids, their specific rotatory power is not greatly influenced, since these acids are almost completely dissociated in aqueous solution; with weak acids, however, the salts are only slightly dissociated and hence the rotatory power is different, being due to very different ions.

A. Pictet (1906) regards the alkaloids not as assimilation products of the organism, but rather as nitrogenous decomposition products of proteins, nucleins, chlorophyll, &c., which have condensed with other substances present in the plants. It is supposed that alkaloids containing the pyrrole group have their origin in protein or chlorophyll, in which such group is certainly present, while those with a pyridine grouping have a similar origin, the transformation of the pyrrole into the pyridine nucleus being possible even in the laboratory; the pyridine group itself does not appear to exist in the proteins, chlorophyll, &c.[2]

[1] **Separation and Tests of Alkaloids.** A mixture of these is separated as follows:

I. From the neutral or acid aqueous solution, ether extracts: *digitalin*, *picrotoxin*, and *colchicine*, and from a solution of these the first and last are precipitated by tannin.

II. From the alkaline aqueous solution, ether extracts: *coniine*, *nicotine*, *brucine*, *delphinine*, *narcotine*, *veratrine*, *atropine*, *strychnine*, *aconitine*, *quinine*, *codeine*, and *physostigmine*.

III. From the alkaline aqueous solution, chloroform extracts: *cinchonine*, *caffeine*, *curarine*, *morphine*, *solanine*, and *theobromine*.

The separate alkaloids can be distinguished by the following colorimetric tests, arranged by Hager. The colours are represented shortly (as with the colouring-matters; *see later*) as follow: *O* = orange; *B* = blue; *Br* = brown; *D* = decolorised or colourless; *Y* = yellow; *Gr* = grey; *Bl* = black; *R* = red; *r* = rose; *Gn* = green; *V* = violet; + = intense; − = weak. The reagents most commonly used are:

(1) *Erdmann's reagent*: to 20 drops of a solution containing 10 drops of HNO_3 (sp. gr. 1·153) and 20 c.c. of water are added 40 c.c. of concentrated H_2SO_4. One cubic centimetre of this liquid is poured on to 1 to 2 grms. of the dry aklaloid and the changes observed after 15 to 30 minutes.

(2) *Fröhde's reagent*: 0·5 grm. sodium molybdate in 100 c.c. conc. H_2SO_4.

(3) *Mandelin's reagent*: 1 grm. ammonium vanadate in 200 grms. H_2SO_4 (monohydrate).

(4) *Marquis's reagent*: a solution of formalin in sulphuric acid.

(5) *Lafon's reagent*: sulphuric acid solution of ammonium selenite.

See Table on p. 628.

[2] **Synthesis of Alkaloids and Medicine.** Even during the most remote ages human beings sought remedies for their ailments in the principles contained in various plants and animals. Galen (A.D. 131–200) studied various medicines more rationally than had been previously done by Hippocrates (400 B.C.).

Numerous medicines proposed by Galen were used as sovereign remedies for some centuries, until indeed Paracelsus (1493–1541) gave a new direction to medicine by contesting the theory of Galen and of Avicenna and by founding *iatrochemistry*, which had such a large following in the Middle Ages, and which ultimately degenerated into the most fantastic sorcery (*see* History of Chemistry, vol. i, p. 14).

Modern chemistry alone could yield medicine any real support, by rigorous control of the physiological and chemical actions of all the natural and artificial drugs.

In the past the curative properties of various substances were discovered by pure chance; this was the case, for instance, with antifebrin (acetanilide), which was administered to a patient in mistake for naphthalene. But nowadays a rational procedure is followed, use being made either of analogy in chemical constitution between the substance under consideration and others of known action or of systematic physiological tests, first on animals and afterwards on human beings.

Until the beginning of the nineteenth century, the energies of chemists were directed to the discovery of the active and essential principles of those parts of plants successfully applied in medicine. When these were isolated in the pure state, attempts were made to establish their chemical structures and, in some cases, to effect their manufacture synthetically.

As early as 1805 Sertürner discovered and isolated *morphine*, the active principle of opium, and in 1821 Pelletier and Caventou discovered the alkaloids of cinchona bark, which were studied in 1850 by Strecker with the object of ascertaining their chemical constitution. The synthesis of these alkaloids was by no means an easy task, but in cases where they themselves have not been obtained by laboratory reactions, simple derivatives have been prepared, and these often exhibit similar therapeutic properties. Thus synthesis has given *codeine* (or methylmorphine) and *dionine* (ethylmorphine), which in many cases are excellent substitutes for morphine, as they are scarcely if at all poisonous. Derivatives of cocaine, such as *eucaine* (a derivative of γ-methoxypiperidine, Ger. Pats. 90,235 and 97,672), and of quinine, such as *euquinine* (the carbethoxy-derivative of quinine, without the bitter taste of the mother-substance), have also been prepared.

Chemical investigation not only gives new products but leads to improved manufacture and consequent cheapen-

Alkaloid	H_2SO_4 conc.	HNO_3 sp gr 1·4	Erdmann's reagent	Frohde's reagent	Mandelin's reagent	Marquis's reagent	Lafon's reagent	2 per cent. aqueous furfural
Aconitine	*Y-Br*; after 24 hours *Br-R*; after 48 hours *D*	*Y*	*Y-Br*; in the hot *R-Br*	*Y-Br*, then *D*	—	—	—	—
Atropine	*D* or *Br*	substance *Br*, solution *D*	*D*	*D*	—	—	—	—
Brucine	− *r*	+*R*, then *O*	*R* and then *Y*	*R*, then *Y*; after 24 hours *D*	—	—	*r*	—
Quinine	*D*	*D*	− *D*	*D* or − *Gn*	—	—	—	—
Quinidine	− *D*	*D*	− *D*	− *D*	—	—	—	—
Cinchonine	*D*	*D*	*D*	*D*	—	—	—	—
Digitalin	*Br* then *R*	− *Br*	*R-Br*, then *R*; after 15 hours +*R*	+*O* then +*R*; in 30 minutes *Bl-Br*; after 24 hours *Gn-Y*	—	—	—	—
Caffeine	*D*	*D*	*D*	*D*	—	—	—	—
Codeine	*D*, after 8 days *B*	*r* then *Y*	*D* then *B*	*Gn* then *B* or after 24 hours − *Y*	*Gn* in hot *B*	*Y*	*Gn*	—
Cocaine	*D*	*D*	*D*	*D*	—	—	—	—
Colchicine	+*Y*	*V* then *B* and *Y*	*Y*	*Y* and −*Gn-Y*	—	—	—	—
Coniine	*D*	*D* then −*Y* then *D*	*D*	*Y*	—	—	—	—
Morphine	*D*, in hot *R* then *V* and *Gn*	*O* then *Y*	−*R* then *Br*	*V*, then *Gn*, *Br*, after 24 hours *V*	—	*R*	*Gn*	*R*
Narcotine	−*Y* then *O* and after 24 hours *r*	*Y* then *D*	*Y*, *O*	*Gr*, then *Br*, *Y*, *r*	*R*	—	*Gn-Br*, in the hot *R*	—
Narceine	*Br* then *Y*	*Y*	*Y* then − *Br*	*Br* then *Y* and *D*	*O*, in the hot *R*	*Y*	*B*, *Br*	—
Nicotine	*D*	*Y* then *R-V* and then *D*	*D*	*Y* then *r*	—	—	—	—
Papaverine	*V* then *B*	*O*	*V* then *B*	*V* then *B* *Y D*	—	—	—	—
Physostigmine	*Y* then *Gn*	—	—	—	—	—	—	—
Piperine	*R* then *O*	*O* and with alkali *R*	− *Y-Br*	*Y* then +*Br Bl*	*Br-Gn*	*R*	*Gn Br*	*Y-Gn* to *GnB*
Solanine	*O*, and after 20 hours *Br*	*D* then −*B*	−*Y*	*R* then *Br* and *Y*	*O*	*Br*	*R-Br*	*R* then *V*
Strychnine	*D* and with bichromate *V*	*Y*	*D*; with MnO_2 *V* then *R*	*D*	*V*	—	—	—
Thebaine	*R* then *O*	*Y*	*R* then *O*	*R* then *O* and *D*	*R*	*R*	—	−*R* then *D*
Theobromine	*D*	*D*	*D*	*D*	—	—	—	—
Veratrine	*O* then *R*	*Y*	*O* then *R*	*Y* then *R*	*R*	*R Br*	—	*V*, in hot *B*
Adrenaline	—	—	—	*Y Br* then *Gn R*	*Y*, *Br*	*R Br*	*Gn*	− *Y*
Berberine	*Gn*	+*R Br*	*Gn*	*Gn-Br*	*B V* then *V Br*	*Y* in hot, *Gn*	*Br Gn*	—
Hydrastine	—	—	—	*Gn Gr*	*R*	—	*Br*	—
Picrotoxin	—	—	—	*O*	*Y Gn*	−*R*	—	—
Digitoxin	—	—	—	*Br*	*Br V*	*r*	*Br V*	*V*

The consumption of alkaloids is growing in all countries. The imports into Italy (exclusive of quinine) amounted to 14,200 kilos in 1908 and 17,320 kilos, of the value of £138,545, in 1910.

CONIINE, $C_8H_{17}N$, is found in hemlock (*Conium maculatum*). For its constitution and syntheses, *see above*.

NICOTINE, $C_{10}H_{14}N_2$, is a strong diacid base which, in combination with malic and citric acids, forms the poisonous alkaloid of tobacco. It is an oil boiling at 247° and possessing a very strong odour; it is soluble in water, alcohol, or ether, and turns brown in the

ing of the old ones. Thus, quinine, which twenty years ago cost £40 per kilo, is now sold in a highly pure state for 32*s*. Vast works now turn out enormous quantities of synthetic drugs, although these are administered in doses of centigrammes; thus, *antipyrine*, discovered by Knorr, was consumed to the extent of hundreds of thousands of kilos in the first few years during which *influenza* made its appearance.

Modern industrial conditions have rendered possible the development of *serotherapy* (*see* p. 115), and great results are now promised by *organotherapy* or *ototherapy*. This is based on the fairly general phenomenon that in the different organs of a healthy individual substances are continually produced capable of guarding them against different affections. This principle, introduced vaguely and confusedly by Brown-Séquard in France in 1891, was in 1895 brought forward with triumph by Baumann, who found that in many persons goitre is due to deficient secretion of iodo-products by the thyroid glands (*see* vol. i, p. 151), and, having extracted the active iodine principle, *thyroidin*, from the thyroid of healthy sheep, that this constitutes a rapid and effective cure for goitre. For the treatment of other diseased organs, *ovarin*, *cerebrin*, *nuclein*, &c., were prepared from the corresponding organs of healthy animals.

Coal-tar derivatives have been employed for the synthesis, not only of artificial alkaloids, antipyretics, and antiseptics, but also of an important group of *anæsthetic* or *hypnotic* substances which have been of great service to medicine and especially to surgery in rendering painless the most complicated operations. At first, substances such as *ether* and *chloroform* were employed which produced *general anæsthesia* of the organism; but the use of these, especially of chloroform, was attended by much inconvenience and often by death of the patient. Sulphuric ether was recognised as an anæsthetic by Faraday as early as 1818, but it was used for the first time by the American doctor, C. W. Long, in 1842.

The anæsthetic is carried by the blood into contact with the nerve-centres which perceive pain, producing a poisoning and a paralysis which last for some time, but at the same time those centres which govern the action of the heart and of respiration are also affected, thus causing the dangers and disturbances accompanying general anæsthesia. The nervous currents start from the periphery, from the points where the surgical operation begins, and are transmitted to the brain, which transforms them into the sensation of pain, and it is precisely by the influence of the anæsthetic on the cerebral centres that pain is avoided. But anæsthesia ceases to be dangerous when the paralysis is effected on the peripheral nerve-centres at the beginning of the nervous currents, without, however, reaching the brain. In this way the idea of *local anæsthesia* was arrived at, this being much more rational and much less dangerous, since by its means only the single organ or region of the body to be operated on is rendered insensible.

To *chloroform*, *ether*, &c., were added, in 1885, *cocaine*, which paralyses only the sensitive peripheral nerves and does not influence the motor nerves. It can now be indicated which specific atomic groupings in the molecules of *anæsthetics or hypnotics* confer on these their special properties.

Hypnotics include those of (1) the chloral hydrate group, to which belong also chloralamide (chloralformamide) and paraldehyde; (2) the tert. amyl alcohol class, $\frac{CH_3}{CH_3}>C<\frac{C_2H_5}{OH}$, characterised by the presence of a hydroxyl and of a carbon atom united to three alkyl groups, the action of these compounds increasing with the molecular weight; (3) the intermediate *dormiol* [tert. amylchloral, $CCl_3 \cdot CH(OH)(OC_5H_{11})$] class; (4) the urethane derivatives, including *hedonal* (methylpropylcarbinol urethane, $NH_2 \cdot CO \cdot O \cdot CH(CH_3)(C_3H_7)$); (5) a group of compounds containing a single carbon atom united to two alkyl groups and to two sulphonic residues, *e.g. trional*, $\frac{CH_3}{C_2H_5}>C<\frac{SO_2 \cdot C_2H_5}{SO_2 \cdot C_2H_5}$ (*methylsulphonal* or diethylsulphonemethylethylmethane); (6) a group studied by E. Fischer and consisting of urea derivatives, *e.g.* $NH_2 \cdot CO \cdot NH \cdot CO \cdot CH(C_2H_5)_2$ (*diethylacetylurea*) or, better, *diethylmalonylurea*, $CO<\frac{NH \cdot CO}{NH \cdot CO}>C<\frac{C_2H_5}{C_2H_5}$ (diethylbarbituric acid), which bears the name of *veronal* (m.pt. 191°; it was prepared by E. Fischer and J. Mering, patented by Messrs. Merck in 1903 and then made by Messrs. Fr. Bayer, of Elberfeld) and serves to replace chloroform, being free from the dangerous consequences of the latter (provided that it is not administered to patients with weak kidneys). Change of the alkyl groups in veronal is accompanied by change in the properties; thus, dimethylbarbituric acid has no hypnotic properties, dipropylbarbituric acid is more effective than veronal, while dibenzylbarbituric acid is without action, possibly owing to its slight solubility.

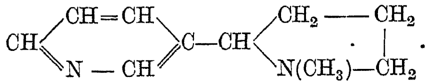
According to H. Meyer and Overton, all substances capable of dissolving fats are more or less anæsthetic, and according to Nicloux (1909) the substance of the nervous system contains an abundance of *lipoids*, *i.e.* of compounds soluble in the same solvents as fats and hence capable of fixing the anæsthetics (they may contain nitrogen and also phosphorus). Thus the quantity of anæsthetic fixed by the organism and hence effective is directly related to the quantity of lipoids present in the various parts of the body. It is also interesting that structural isomerism produces marked change in the physiological action, *tropacocaine*, for instance, being an anæsthetic, while *benzoyltropine* acts as a mydriatic.

Of the numerous other anæsthetics, *orthoform* (methyl ester of m-amino-p-hydroxybenzoic acid), *alipine* *holocaine*, may be mentioned.

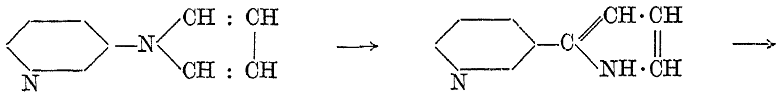
But in order that local anæsthesia may be efficacious and lasting, it is necessary to prevent the anæsthetic inoculated at a certain place from being carried away (*resorbed*) by the blood, and this was at first attained by causing the venous blood at that place to stagnate by preventing circulation. The same end was reached later by intense local cooling produced by the rapid evaporation of *ethyl* or *methyl chloride*.

For internal surgical operations (*e.g.* in the thorax, &c.), *adrenaline*, $C_6H_3(OH)_2 \cdot CH(OH) \cdot CH_2 \cdot NH \cdot CH_3$, is of the greatest use, as it produces considerable contraction of the blood-vessels without driving all the blood from them, although it prevents fresh blood from arriving; the anæsthetic can thus be kept as long as is desired in the inoculated region. The substitution of cocaine by *stovaine* (less poisonous) leads to partial *spinal anæsthesia* or medullary anæsthesia, which now permits the most difficult surgical operations on the abdominal organs and even renders possible painless childbirth.

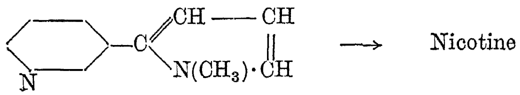
air. When oxidised by permanganate it forms nicotinic acid, and as further it contains also a pyrrolidine group, its constitution is represented as follows:



Synthetically it is obtained from β-aminopyridine which is converted into its mucic cid salt, and then passes through the following stages:



N : β-Pyridylpyrrole α : β-Pyridylpyrrole



Nicotyrine

Practically it is prepared from ordinary tobacco extract, by diluting, rendering strongly alkaline with NaOH, and extracting with ether. From the ethereal solution, the alkaloid is extracted by shaking with dilute sulphuric acid and decanting off the acid solution. The latter is again made strongly alkaline and shaken with ether, and the ethereal solution dehydrated by means of solid NaOH. The ether is then distilled off and the remaining nicotine distilled in a stream of hydrogen.

It is a very powerful poison and is used medicinally to counteract nervous irregularity of the heart and is employed in agriculture, as tobacco extract, to kill insects.[1] Impure 75 per cent. nicotine costs 148*s*. per kilo, and the pure product 184*s*.

[1] Tobacco is a herbaceous plant, originally an annual but now sometimes a biennial, of the order Solonaceæ (*Nicotiana tabacum*), which includes about fifty species and sub-species of American origin, *e.g.* the Virginia tobacco plant (*Nicotiana tabacum, see* Fig. 420), the Maryland large-leaved tobacco (*N. latissima, N. rustica, N. suffruticosa,* &c.). These grow well in various countries, as is shown by the following Table, giving the mean production of raw tobacco a few years ago (the figures given are tons):

	Output	Imports less Exports	Exports less Imports		Output	Imports	Exports
United States	250,000	—	115,000	Dutch Indies	34,000	—	18,000
British India	185,000	—	—	Japan	26,000	—	—
Austria-Hungary	70,000	14,000	—	France	25,000	23,000	—
Russia	58,000	—	5,000	Cuba	24,000	—	13,500
Turkey	40,000	—	14,000	Philippines	22,000	—	12,000
Germany	37,000	45,000	—	Brazil	17,000	—	11,000
(*a*) Belgium, (*b*) Algeria, (*c*) Australia, (*d*) Porto Rico, (*e*) Roumania, (*f*) San Domingo, (*g*) Ceylon, each about	5,000	(*a*) 10,000 (*c*) 5,000 (*e*) 1,300	(*d*) 4,500 (*f*) 3,000 (*g*) 3,000	Greece	9,000	—	5,000
				(*a*) Bosnia, (*b*) Netherlands (*c*) Argentine, (*d*) Cochin China, (*e*) Mexico, each about	3,300	(*c*) 5,200	
(*a*) Italy, (*b*) Switzerland, (*c*) Servia, (*d*) Sweden, each from 1500 to	2,300	(*b*) 5,000 (*c*) 1,000 (*d*) 4,300		(*a*) China, (*b*) Paraguay and other countries, together	120,000		(*a*) 5,500 (*b*) 5,000
				England	—	50,000	

Italy imports about 2000 tons of tobacco leaf (about £1,080,000) and exports manufactured tobacco to the value of about £200,000.

The world's production of raw tobacco varies from 900,000 to 1,000,000 tons, of the value of £48,000,000 to £56,000,000. The price is about £32 to £40 per ton for the ordinary quality and £120 to £160 for the finer qualities (Manila, Havana, Sumatra).

Ordinary tobacco plants are only slightly branched and have a height of about 1 metre, although some exceed 1½ metre. They are studded with sticky hairs, and the leaves are wide and oval or, sometimes, long and narrow, as with Chinese tobacco (*N. chinensis*). The flowers are in clusters and resemble those of potatoes, but are usualy flesh-red. The cultivation of tobacco requires a good soil rich in humus, and the climate, soil, and mode of growing exert a considerable influence on the quality of the tobacco. The readiness with which a tobacco burns in the form of cigars depends on the potash-content of the plant, while chlorides hinder the combustion. On this account fertilisation with stable manure, sewage, or potassium chloride is avoided, preference being given to potassium or ammonium sulphate mixed with a little Thomas slag and stable manure. The young plants from the forcing

ATROPINE, $C_{17}H_{23}O_3N$, is the alkaloid of the berries of *Atropa belladonna* (deadly nightshade) and of the fruit of *Datura stramonium* (thorn-apple). In dilute solution it is used as a mydriatic (enlarging the pupil of the eye) and as an analgesic (relieving pain). It is somewhat poisonous and melts at 115·5°. As the products of the decomposition of atropine in various ways comprise heptamethylene derivatives, substituted pyrrolidines and piperidines, **Tropine**, $NC_8H_{15}O$, and **Tropic Acid** [$C_9H_{10}O_3$, or α-phenyl-β-hydroxypropionic acid, $OH \cdot CH_2 \cdot CH(C_6H_5) \cdot CO_2H$], atropine is regarded as an ester, a tropate of

house are planted out in about March, and at the beginning of July the dry and dirty leaves near the soil are detached, together with the useless branches and the flowers. The other, useful leaves are then removed as they begin to yellow and are dried on strings or in steam drying-ovens, and are then sorted and tied in bundles.

In January the leaves are placed in heaps so as to induce fermentation, which renders them brown and gives them flavour

The leaves arrive at the factory in cloth bales. They are first sorted into kinds suitable for different types of tobacco and are then beaten to remove sand and dust. They are then arranged in layers, each of which is sprinkled with 5 to 10 per cent salt solution (it is this which renders cigars hygroscopic) to soften it, to facilitate the subsequent operations and to prevent putrid fermentation. In this state it is sometimes placed in tepid apartments to initiate a second fermentation, which refines the milder qualities; in some cases this end is attained by washing with dilute solutions of salts, alkali, or acid, or, more rarely, by torrefying at 60° to 70°.

The best flavour and aroma are obtained, however, by *curing*, *i.e.* by immersing the leaf in an aqueous solution of saccharine substances, various drugs, nitre, colouring-matters, aromatic substances, alcohol, &c. (each manufacturer has his particular method of curing); the drained or pressed leaves are then left in heaps for a longer or shorter time until they are uniformly soaked.

By suitable machines the ribs of the leaves are either cut or beaten off and the cut leaves then dried by heating in revolving metal drums; the dried leaves are rapidly cooled in a current of air, &c. The subsequent operations for the preparation of cigars, cigarettes, cut tobacco for pipes, or snuff are merely mechanical and need not be described here.

Mention may, however, be made of recent attempts to diminish the harmful effects of tobacco, which is now smoked in every country in the world. It seems that when the Spaniards invaded America, the use of tobacco was already known in that country, and they not only extended its use there but introduced it into Europe (by the Thévet brothers in 1517), arousing grave apprehension owing to a statement by the medical men that it was highly injurious to health. In 1613 Tsar Michael Federowitz prohibited its use in his territory under penalty of death or of the cutting off of the nose. James of England published in 1619 a decree forbidding the use of tobacco and describing smoking as a "habit disgusting to the sight, nauseating to the smell, dangerous to the brain, harmful to the heart, and spreading around the smoker repugnant exhalations." In 1660 the Senate of Berne punished the use of tobacco like robbery or homicide, and in 1623 Amurat IV prohibited its use by the Turks in order that they might not become intoxicated or infertile. But to human nature the forbidden fruit is the most desired, and, being useless, is none the less necessary. The employment of tobacco spread rapidly everywhere, and many states, to limit its consumption, imposed enormous taxes on tobacco, and ended by making it a Government monopoly and thus deriving a vast income to the Treasury.

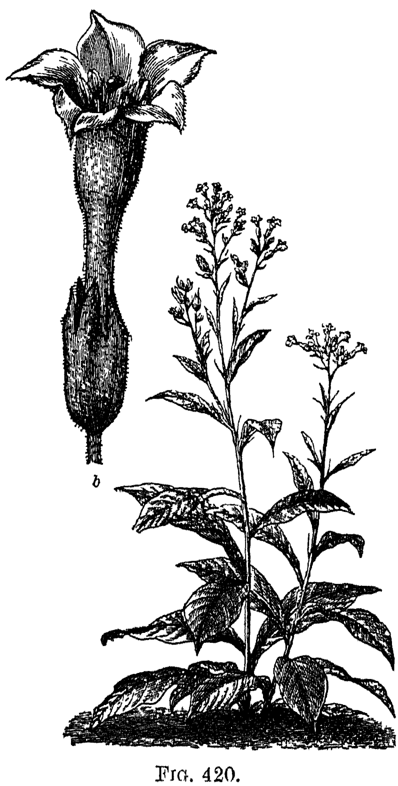


FIG. 420.

Since then no Government has occupied itself with the health of its subjects, the only care being the enlargement of the Exchequer. In Italy, after the partnership between the Government and a private company from 1868 to 1883, the trade in tobacco became a monopoly of the State, which derives from it a net annual income of about £7,000,000.

The mean yearly consumption of tobacco per head is as follows: North America, 3·1 kilos; Netherlands, 2·5; Belgium, 2 8; Switzerland, 2·3; Germany, 1·5; Austria-Hungary, 1·5; Sweden, 1·2; Russia, 0·9; Servia, 0 8· France, 0·8; England, 0·7; Italy, 0·6; Roumania, 0·2; Denmark, 0·1; Finland, 0·1.

The harm caused by tobacco is due especially to the nicotine, to which man becomes accustomed without serious inconvenience, in the same way as to change of climate, food, drink, or other conditions. Attempts have been made in recent years to render tobacco less injurious by extraction of the nicotine with one of a number of solvents, but such treatment results in the removal of the aromatic substances of the tobacco (*see also* Ger. Pats. 178,962, 197,159, and 212,417 of 1908).

Better results are obtained by filtering the smoke through fibres or textile materials before it reaches the mouth. Thus the Thoms process (Ger Pat. 145,727), which has proved very satisfactory, consists in arranging in the mouthpiece of the pipe a small plug of cotton-wool impregnated with ammoniacal ferric chloride or ferrous sulphate, this retaining all the burning ethereal oils, the hydrogen sulphide, a considerable proportion of the hydrocyanic acid, and almost all the nicotine and its basic derivatives in the smoke. Treating the raw tobacco with ozone has also been employed with the view of facilitating the elimination of the nicotine, increasing the combustibility, and improving the quality. The aroma of tobacco is also intensified by the addition of small quantities of methyleugenol and methylisoeugenol.

tropine, the structure of the latter (which has also been prepared synthetically) being,

```
CH2—CH———CH2 (α)
|     |      |
|    N·CH3  CH·OH   (m.pt. 62° ; b.pt. 220°).
|     |      |
CH2—CH———CH2 (α)
```

Hyoscyamine, stereoisomeric with atropine, melts at 109°.

Tropine, formed by the splitting of atropine with barium hydroxide, is a tertiary base containing a secondary alcoholic group and is therefore known also as *tropanol*. When oxidised with chromic acid, it forms first a ketone, **Tropinone**, $C_8H_{13}ON$, and then **Tropinic Acid**, $CH_3N : C_4H_6(CO_2H)(CH_2 \cdot CO_2H)$, owing to the rupture of the piperidine ring. With concentrated HCl, tropine forms **Tropidine** (or *tropene*), $C_8H_{13}N$, which is obtained also by elimination of CO_2 from anhydroecgonine and forms an oily base, b.pt. 162°.

OTHER ALKALOIDS are: **Veratrine** (*cevadine*), $C_{32}H_{29}O_9N$, found in *Veratrum album*; **Sparteine**, $C_{15}H_{26}N_2$, found in *Sparticum scoparium;* **Sinapine**, $C_{16}H_{25}O_6N$, found in the seeds of white mustard and derived from choline and from **Sinapic Acid** (*dimethyl-trihydroxycinnamic acid*), $C_{11}H_{12}O_5$; **Hydrastine**, $C_{21}H_{21}O_6N$, obtained from the roots of *Hydrastis canadensis*, has similar properties to the alkaloid from *Secale cornutum* and gives **Hydrastinine**, $C_{11}H_{11}O_2N,H_2O$, on oxidation.

MORPHINE, $C_{17}H_{19}O_3N$. The latex of the capsule of *Papaver somniferum* when condensed forms opium, which, along with various other compounds (*see* next page), contains considerable quantities of *morphine* (about 10 per cent.).[1] Morphine, melting and decomposing at 230°, is slightly soluble in water and odourless, and possesses narcotic and analgesic properties, being used in medicine as hydrochloride, $C_{17}H_{19}O_3N,HCl,3H_2O$. It is a tertiary base with phenolic characters and, when distilled in presence of zinc dust, gives pyridine, pyrrole, quinoline, and phenanthrene.

Morphine is extracted from opium by means of water, the evaporated aqueous extract being treated with sodium carbonate to precipitate all the alkaloids (about twenty) of the opium; after 24 hours the precipitate is washed with water and then with alcohol, which removes the resins and all the alkaloids excepting nearly the whole of the morphine. The crude morphine remaining is dissolved in acetic acid (which leaves behind the narcotine impurities), the solution filtered through animal charcoal, and the morphine liberated by means of ammonia, washed with cold water and dried. It is obtained in a purer form by repeatedly boiling its alcoholic solution with animal charcoal and recrystallising.

The action of opium is due to the presence of a number of alkaloids, which are divided by A. Pictet into:

(1) The **Morphine Group**, including:

Morphine, $C_{17}H_{17}ON(OH)_2$	*Codeine*, $C_{17}H_{17}ON(OH)(OCH_3)$
Pseudomorphine, $[C_{17}H_{16}ON(OH)_2]_2$	*Thebaine*, $C_{17}H_{15}ON(OCH_3)_2$

(2) The **Papaverine Group**, comprising mainly isoquinoline derivatives, which have a mild physiological action:

Papaverine, $C_{16}H_9N(OCH_3)_4$	*Laudamine*, $C_{17}H_{15}N(OH)(OCH_3)_3$
Laudanidine, $C_{17}H_{15}N(OH)(OCH_3)_3$	*Laudanosine*, $C_{17}H_{15}N(OCH_3)_4$
Codamine, $C_{18}H_{18}ON(OH)(OCH_3)_2$	*Cryptopine*, $C_{19}H_{17}O_3N(OCH_3)_2$
Narcotine, $C_{19}H_{14}O_4N(OCH_3)_3$	*Oxynarcotine*, $C_{19}H_{14}O_5N(OCH_3)_3$
Protopine, $C_{20}H_{19}O_5N$	*Narceine*, $C_{20}H_{18}O_5N(OCH_3)_3$
Tritopine, $(C_{21}H_{27}O_3N)_2O$	*Meconidine*, $C_{21}H_{23}O_4N$

[1] **Estimation of Morphine in Opium.** Of the various methods, that of Stevens (1902) gives good results: 4 grms. of powdered opium are mixed in a mortar with 2 grms. of fresh calcium hydroxide and 10 grms. of water; an additional quantity of 19 c.c. of water is then introduced, the whole being mixed for half an hour, and filtered Exactly 15 c.c. of the filtrate are mixed in a 60 c.c. bottle, with 4 c.c. of alcohol and 10 c.c. of ether, 0·5 grm. of ammonium chloride being then added and the bottle shaken for 30 minutes, stoppered, and left at rest in a cool place for 12 hours. The mass is then poured on to a filter containing a tuft of cotton-wool to retain the morphine crystals. The bottle and funnel are washed with water saturated with morphine until the filtrate becomes colourless. The funnel is now placed over the bottle, the cotton lifted with a glass rod drawn out to a curved point, and the crystals rinsed into the bottle with 12 c.c. of N/10-sulphuric acid; the cotton is then also put into the bottle, which is corked and well shaken. After rinsing both cork and funnel with water, the excess of acid is titrated with N/10-caustic soda, using as indicator a solution of *iodo-eosin* (*eosin blue*) or litmus. Multiplication of the number of cubic centimetres of acid fixed by the morphine by 1·5038 gives the percentage of morphine in the opium, but this number must be increased by 1·12 to compensate for the morphine remaining in solution.

Papaveramine, $C_{21}H_{21}O_5N$	*Gnoscopine*, $C_{22}H_{33}O_7N$
Santaline, $C_{37}H_{36}O_9$	*Hydrocotarnine*, $C_{11}H_{12}O_2N(OCH_3)$
Lautopine, $C_{23}H_{25}O_4N$	*Berberine*, $C_{20}H_{17}O_4N$

Opium contains also **Meconic Acid**, $C_7H_4O_7$, in combination with various alkaloids, and further: wax, proteins, caoutchouc, pectic and gummy matters, lactic and sulphuric acids, ammonium salts, &c.

Good opium contains 8 to 24 per cent. of water, 3·5 to 5 per cent. of ash, 45 per cent. of aqueous extract, 9 to 15 per cent. of morphine, about 5 per cent. of narcotine, 0·8 per cent. of papaverine, 0·4 per cent. of thebaine, 0·3 per cent. of codeine, and 0·2 per cent. of narceine.

The price of good opium is 28*s*. to 32*s*. per kilo, pure crystalline morphine costing £24 and its hydrochloride £18 per kilo. In 1905 Germany imported 687 quintals of opium of the value of £65,200. China imported 26,000 quintals in 1908, about 25,000 in 1909, and nearly 20,000 in 1910.

In 1909 England imported 200 tons of opium (£269,695) and in 1910 300 tons (£434,064), while in 1911 the exports were of the value of £78,982. The United States imported 190 tons (£273,800) in 1910 and 300 tons (£552,000) in 1911.

COCAINE, $C_{17}H_{21}O_4N$, with other alkaloids, constitutes the active part of the leaves of *Erythroxylon coca*. It is lævo-rotatory, melts at 98°, has an analgesic action and serves also to produce local anæsthesia (Koller, 1884).

Strong acids in the hot decompose it into methyl alcohol, benzoic acid and *ecgonine*, $C_9H_{15}O_3N$(Lossen, 1865), which is the α-carboxyl derivative of tropine (*see above*), and, as with methyl alcohol and benzoic acid it gives cocaine again, the latter must contain the groups $C_9H_{13}O_2N\begin{cases}OCH_3\\COC_6H_5\end{cases}$; confirmation of this is given by the synthesis (rather a complicated one) of cocaine. The constitution of cocaine is as follows (Willstätter, 1898):

$$\begin{array}{lll}CH_2\text{—} & CH\text{———} & CH\cdot CO_2CH_3\\ | & | & |\\ | & N\cdot CH_3 & CH\cdot CO_2C_6H_5\\ | & | & |\\ CH_2\text{—} & CH\text{———} & CH_2\end{array}$$

; the characteristic group (*anæsthesiophore*) is the benzoyl residue, while elimination of the methyl group united to the nitrogen atom or of the CO_2CH_3 group scarcely affects the anæsthetic properties. On the other hand, almost all the aminohydroxybenzoic esters are *mild local anæsthetics* (Einhorn and Heinz, 1897), *e.g.* *anæsthesin* or ethyl p-aminobenzoate, $NH_2\cdot C_6H_4\cdot CO_2C_2H_5$. The anæsthetic characters of these substances are intensified if, in place of NH_2, $N(CH_3)_2$ groups are present, preferably joined to other methyl groups. This is the case, for instance, in:

$$\underset{\text{Stovaine}}{\begin{array}{c}C_6H_5\cdot CO_2\diagdown\quad\diagup CH_3\\ C\\ C_2H_5\diagup\quad\diagdown CH_2\cdot N(CH_3)_2\end{array}} \quad\text{and}\quad \underset{\text{Alipine}}{\begin{array}{c}C_6H_5\cdot CO_2\diagdown\quad\diagup CH_2\cdot N(CH_3)_2\\ C\\ C_2H_5\diagup\quad\diagdown CH_2\cdot N(CH_3)_2\end{array}}$$

prepared by Messrs. Bayer in 1905. Both of these are less poisonous than cocaine, but have not its property of contracting the blood-vessels. They are therefore mixed with *adrenaline*, which shows this property in a marked degree and also diminishes the toxicity of certain alkaloids, especially of cocaine.

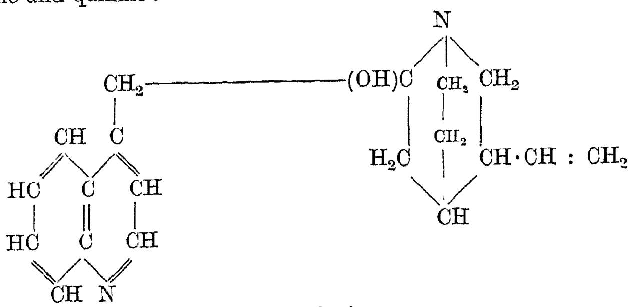
NARCOTINE, $C_{22}H_{23}O_7N$, exists to the extent of 6 per cent. in opium, melts at 126°, and is a slightly poisonous, weak, tertiary base containing three methoxyl groups. When hydrolysed, narcotine gives **Meconic Anhydride**, $C_{10}H_{10}O_4$, and **Cotarnine**, $C_{12}H_{13}O_3N$, which is a derivative of isoquinoline (*see later*), and with bromine gives dibromopyridine.

STRYCHNINE, $C_{21}H_{22}O_2N_2$, is present, with **Brucine**, $C_{23}H_{26}O_4N_2$, and **Curarine**, in the seeds of *Strychnos nux vomica*. They are very powerful poisons, which, even in small doses, cause death, accompanied by tetanic muscular contorsions; curarine is used as an antidote to the other two alkaloids. Strychnine melts at 265°, and is a mono-acid tertiary base slightly soluble in water; it gives indole and quinoline when fused with potash and β-picoline on distillation with lime.

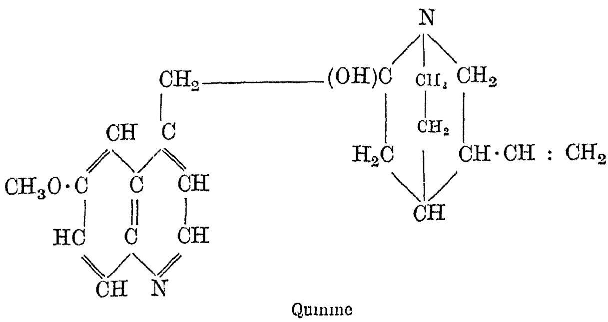
QUININE, $C_{20}H_{24}O_2N_2$. The bark of various species of cinchona has yielded, up to the present, twenty-four alkaloids, the most important being quinine and **Cinchonine**,

$C_{19}H_{22}O_2N_2$, both of these possessing in different degrees febrifugic properties. The other alkaloids include **Hydroquinine**, $C_{20}H_{26}O_2N_2$; **Cinchonidine**, $C_{19}H_{22}ON_2$; **Hydrocinchonidine**, $C_{19}H_{24}ON_2$; **Quinidine**, $C_{20}H_{24}O_2N_2$, &c.

Quinine is lævo-rotatory, slightly soluble in water and odourless and has an intensely bitter taste; it melts at 177°, or, when crystallised with $3H_2O$, at 57°. It is a di-acid base, containing two tertiary nitrogen atoms capable of salt-formation with two equivalents of acid, then often giving aqueous solutions showing blue fluorescence characteristic of quinine. It contains a hydroxyl and a methoxyl group, and its constitutional formula, although not completely established, must consist of two cyclic systems, $NC_{10}H_{15}(OH)-NC_9H_5\cdot OCH_3$, the first being somewhat analogous to tropine (*see above*) and the second representing 5-methoxyquinoline, which can be obtained by fusing quinine with potash. After protracted investigation, W. Königs (1906–1907) arrived at the following probable structures for cinchonine and quinine:

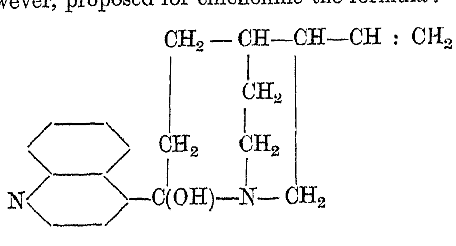


Cinchonine



Quinine

Rabe (1906–1907), however, proposed for cinchonine the formula:



which is in harmony with the Beckmann oxime reaction.

Oxidation of quinine gives, among other products, **Quinic Acid**, $C_9H_5N(OCH_3)\cdot CO_2H$.

To combat fever, especially malarial fever, use is made of the *normal sulphate of quinine*, $(C_{20}H_{24}O_2N_2)_2,H_2SO_4,8H_2O$ (from alcohol it crystallises with $2H_2O$), or of *quinine hydrochloride*, $C_{20}H_{24}O_2N_2,HCl,2H_2O$, which is far more readily soluble in water.

Quinine bisulphate or acid sulphate contains 1 mol. of quinine per 1 mol. of sulphuric acid.

Quinine is extracted from the finely ground bark by mixing it with lime and extracting with hot mineral oils (paraffin oil, &c.) of high boiling-point. From this solution the alkaloid is obtained by shaking with dilute sulphuric acid, neutralisation of the acid solution with sodium carbonate in the hot resulting in the crystallisation of most of the quinine

as sulphate from the cold solution, the other alkaloids remaining dissolved. From the sulphate the quinine is liberated by means of ammonia.

The purification of quinine is not easy and is sometimes effected by precipitating it from solution as tartrate by addition of Rochelle salt.

Statistics. Quinine bisulphate costs about 28*s*. per kilo; the sulphate 32*s*.; and the hydrochloride 40*s*. Of the world's output of cinchona bark, 90 per cent. comes from Java, which in 1900 exported 60,000 quintals, and in each year from 1905–1909 more than 80,000 quintals of the bark, giving 6 to 6·5 per cent. of quinine sulphate.

In 1898 Germany imported 3537 tons of cinchona bark, worth about £128,000; in 1905 the imports amounted to 2594 tons, of the value of £168,000, and in the same year Germany exported 1404 quintals of quinine and its salts, of the value of £224,000, and 461 quintals of other alkaloids, of the value of £424,000: in 1907 the exports were 1700 quintals and in 1908 about 1500 quintals at 22*s*. per kilo.

England imported 1080 tons (£35,759) of cinchona bark in 1909, 1123 tons (£39,520) in 1910, and 1020 tons (£37,169) in 1911, while the imports and exports of *quinine salts* were as follow:

	Imports	Exports
1909	£82,556	£55,065
1910	90,771	56,866
1911	98,056	75,080

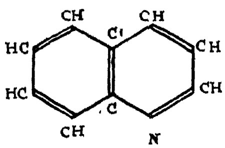
The United States imported 1500 tons (£52,200) of cinchona and similar barks in 1910 and 1550 tons (£55,000) in 1911; also quinine salts and alkaloids to the value of £76,400 in 1910 and £95,400 in 1911.

In 1904 Italy imported 1627 quintals (in 1908, 1384) of cinchona bark of the value of £13,650. In 1878, at the time of the Fabrica Lombarda of quinine in Milan, Italy consumed 10,000 kilos of quinine (5000 furnished by the Fabrica Lombarda, which also sent 20,000 kilos, at £28 to £32 per kilo, to Russia). After 1902, in consequence of the valuable studies of Ross, Grassi, and Celli on *malaria* (a disease which is transmitted by the *Anopheles* mosquito and against which a couple of small doses of quinine per week render one immune), a Government monopoly was instituted to distribute quinine cheaply or gratuitously in the malarial centres. The beneficial results obtained are shown by the following figures: in 1902–1903 the consumption of quinine distributed in this way was 2242 kilos; in 1903–1904 7234 kilos; in 1904–1905 14,071 kilos; in 1905–1906 18,712 kilos, and in 1906–1907 21,723 kilos. The mortality from malaria, which was 21,000 in 1887 and 15,865 in 1900, fell to 9908 in 1902, to 8513 in 1903, to 8501 in 1904, to 7838 in 1905, and to 4690 in 1906. In addition to these advantages, the Italian Government made in 1906 a profit of more than £1400 from its commerce in quinine. There is now scarcely any quinine made in Italy, but the imports amount to 30,000 to 40,000 kilos, 20,000 to 30,000 kilos being converted into pastilles and sold practically at cost price to combat malaria.

5. QUINOLINE AND ITS DERIVATIVES

Quinoline and pyridine are related in the same way as naphthalene and benzene.

QUINOLINE, C_9H_7N, *i.e.*



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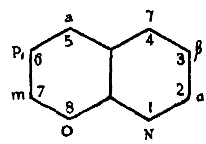
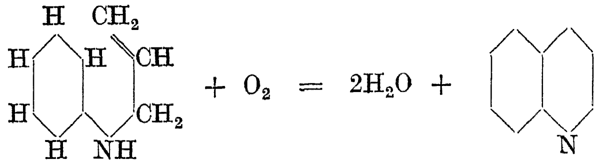


, is a highly refractive, colourless liquid of peculiar odour and is found in bone tar and also in coal-tar, but is now prepared in the pure state by Skraup's synthesis.

It is slightly soluble in water, has the sp. gr. 1·1081 at 0°, boils at 236° and functions as a tertiary base (the nitrogen not being combined with nitrogen). With acids it forms salts, *e.g.* the bichromate $(C_9H_7N)_2H_2Cr_2O_7$.

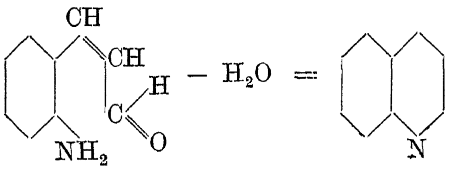
Its constitution is deduced from the following syntheses :

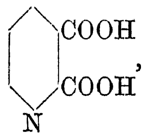
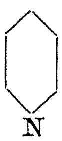
(1) By the interaction of **Allylaniline** and PbO_2 at a red heat :



(2) Skraup obtained it by heating aniline with glycerol, sulphuric acid, and nitrobenzene; in this way acroleïn is formed, which then gives **Acroleïn-aniline**, $C_6H_5 \cdot N : CH \cdot CH : CH_2$. The nitrobenzene acts purely as an oxidising agent and can be replaced by As_2O_3.

(3) o-Nitrocinnamaldehyde on reduction gives o-aminocinnamaldehyde, which loses 1 mol. H_2O and yields quinoline, the fact that the latter is an ortho-derivative of benzene being thus proved :



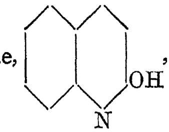
When quinoline is oxidised, the benzene nucleus is attacked first, with formation of a dibasic **Quinolinic Acid**, , which gives pyridine, , when distilled with lime. Hence, as was suggested long ago by Körner, quinoline contains a benzene and also a pyridine nucleus. It is analogous to naphthalene, one α-CH group being replaced by a nitrogen atom. That the linkings in quinoline are, at least in part, olefinic double bonds is shown by the behaviour of this compound to ozone.

Quinoline forms many isomeric derivatives, seven monosubstituted, twenty-one disubstituted, and still more trisubstituted compounds being possible.

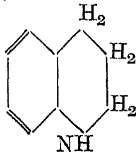
The positions of the replaceable hydrogen atoms are indicated by numbers or by the letters α, β, and γ for the pyridine nucleus and o, m, p, a (ortho-, meta-, para-, ara-) for the benzene nucleus.

The constitution of quinoline derivatives can be determined by means of the general synthesis of Skraup, variously substituted anilines with the substituents in the benzene nucleus being used; or often by oxidation, which usually attacks the benzene nucleus and not the pyridine nucleus, so that it is easily ascertained whether the substituent is in the one or the other nucleus.

The *sulpho-acids* (or sulphonic acids) of quinoline, when fused with KOH, give *hydroxy-quinolines*, and these, on being heated with KCN, form *cyanoquinolines*, which are converted by hydrolysis into the corresponding *quinolinecarboxylic acids*,—those containing the carboxyl in the benzene nucleus are called *quinolinebenzocarboxylic acids*. Oxidation of cinchonine gives *cinchonic acid*, $C_9H_6N \cdot CO_2H$ (m.pt. 254°), which is *quinoline-γ-carboxylic acid*, and from this is derived *quinic acid* (*see above*), $C_9H_5N(OCH_3) \cdot CO_2H$ (p : γ), consisting of yellow prisms melting at 280°. When acridine is oxidised it yields *quinoline-$\alpha \cdot \beta$-dicarboxylic acid* or *acridic acid*.

Carbostyril is 2-Hydroxyquinoline, 

, and has the character of the phenols, dissolving in alkali and being reprecipitated by CO_2, &c.

When quinoline is reduced with nascent hydrogen, this unites with the nitrogenated nucleus, forming **Tetrahydroquinoline**, $C_9H_{11}N$, or 

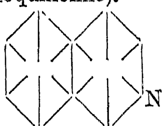
, which behaves as a secondary aromatic amine ($>$NH).

If the reduction is pushed further, the hydrogen is added also to the benzene nucleus, forming *decahydroquinoline*, $C_9H_{17}N$, which behaves like an aromatic amine.

Quinaldine or α-**Methylquinoline**, $C_{10}H_9N$, is found in coal-tar and boils at 246° ; with phthalic anhydride it gives a fine colouring-matter, **Quinoline Yellow**, $C_{10}H_7N(CO)_2C_6H_4$.

When quinoline is heated with metallic sodium it gives *diquinolyl*, $C_9H_6N \cdot C_9H_6N$, analogous to dipyridyl and diphenyl. Polymerisation of quinoline yields *diquinoline*, $(C_9H_7N)_2$, crystallising in yellow needles.

METHOXYQUINOLINE, $C_9H_6N \cdot OCH_3$, corresponding with anisole, resembles quinoline ; among its derivatives are the antipyretic, **Thalline**, $C_9H_{10}N \cdot OCH_3$, and **Analgen** (o-ethoxy-α-benzoylaminoquinoline).

ISOQUINOLINE, C_9H_7N or 

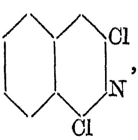
, is a colourless liquid boiling at 237°, melting at 21° and forming a slightly soluble sulphate.

It is obtained from tar and also synthetically by heating the ammonium salt of homophthalic acid :

$$C_6H_4\left<\begin{matrix}CH_2 \cdot COONH_4 \\ COONH_4\end{matrix}\right. = 2H_2O + NH_3 + C_6H_4\left<\begin{matrix}CH_2 \cdot CO \\ | \\ CO \cdot NH\end{matrix}\right. ,$$

Homophthalimide

which with $POCl_3$ gives $C_6H_4\left<\begin{matrix}CH_2 \cdot CCl_2 \\ | \\ CCl_2 \cdot NH\end{matrix}\right.$, and elimination of 2HCl from this yields

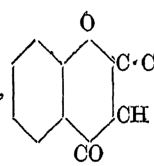


, *i.e.* dichloroisoquinoline.

When oxidised it gives phthalic acid and **Cinchomeronic Acid**, $C_5H_3N(CO_2H)_2$ (a pyridine derivative).

Since it does not fix ozone, it must be assumed, contrary to the former view, that it does not contain olefinic double linkings, but that centric bonds are probably present in both nuclei (Molinari, 1907).

Other condensed nuclei, similar to quinoline, are as follow :

CHROMONE, $C_6H_4\left<\begin{matrix}O \cdot CH \\ \| \\ CO \cdot CH\end{matrix}\right.$, of which the β-methyl-derivative, 

, m.pt. 71°, is well known.

FLAVONE, the phenyl-derivative of *chromone*, $C_6H_4\left<\begin{matrix}O \cdot C \cdot C_6H_5 \\ \| \\ CO \cdot CH\end{matrix}\right.$, melts at 97°, and occurs as hydroxy-derivatives in many glucosides, to which it imparts the yellow coloration.

Thus it occurs in *quercetin* (or *flavin*), which is a pentahydroxyflavone, while with isodulcitol it forms the glucoside **Quercitrin**, $C_{21}H_{23}O_{12}$, obtained from tea, hops, and the bark of *Quercus tinctoria* (*morin* is an isomeride of quercetin, and is found in *Maclura tinctoria*). **Chrysin**, $C_{15}H_{10}O_4$, is a dihydroxyflavone found in poplar buds; **Luteolin**, $C_{15}H_{10}O_6,2H_2O$, is a tetrahydroxyflavone, and forms the colouring-matter of *Reseda luteola*, while *apigenin* is a glucoside of trihydroxyflavone, and is found in parsley and celery.

Of numerous dyestuffs formed by the condensation of heterocyclic groups, mention will be made later in the chapter on *colouring-matters*, but a group of substances with heterocyclic nuclei and intimately connected with indigo will be considered here.

ISATIN, $C_6H_4<\substack{NH\\CO}>CO$, forms reddish yellow prisms soluble in alcohol and in hot water, and may be regarded as the *lactam* (*see* p. 355) of **Isatinic Acid**, $NH_2\cdot C_6H_4\cdot CO\cdot COOH$. It is obtained from o-nitrobenzoylformic acid (*see later*, Indole), by oxidising indigo with nitric acid, &c. It dissolves in KOH, giving first a violet colour ($C_6H_4<\substack{NK\\CO}>CO$), while in the hot it yields potassium isatinate, $C_6H_4<\substack{NH_2\\CO\cdot CO_2K}$. Oxidation of isatin with chromic acid gives rise to **Isatic Acid** (anhydride of anthranilcarboxylic acid), $C_6H_4<\begin{array}{l}NH\cdot CO\\ \qquad\ \ | \\ CO\cdot O\end{array}$.

From **Pseudoisatin**, $C_6H_4<\substack{CO\\N}>C\cdot OH$ (which would be a *lactim*) is derived the methyl ether or **Methylpseudoisatin**, $C_6H_4<\substack{CO\\N}>C\cdot OCH_3$ (red powder). **Methylisatin**, $C_6H_4<\substack{N(CH_3)\\-CO-}>CO$, is also known.

DIOXYINDOLE, $C_6H_4<\substack{CH(OH)\\NH}>CO$, is formed by reducing isatin with zinc and HCl and readily gives isatin again on oxidation. It is the internal anhydride of o-amino-mandelic acid, and exhibits both basic and acid properties. It crystallises in colourless prisms, melting at 180°.

OXINDOLE, $C_6H_4<\substack{NH\\CH_2}>CO$, acts both as an acid and as a base, and hence dissolves in alkali and in HCl. It is the lactam of o-aminophenylacetic acid, and can, indeed, be obtained by reducing o-nitrophenylacetic acid. It forms colourless needles, m.pt. 120°, and forms dioxyindole on oxidation.

INDOXYL, $C_6H_4<\substack{-NH-\\C(OH)}>CH$, is isomeric with the preceding compound, and is formed by fusing indigo with KOH or by the elimination of CO_2 from *indoxylic acid* or *indophore*.

It occurs in the urine of herbivorous animals in the form of **Potassium Indoxylsulphate**, $C_8H_6N\cdot O\cdot SO_3K$ (*indican of the urine*). Derivatives of **Pseudoindoxyl**, $C_6H_4<\substack{NH\\CO}>CH_2$, are also known.

SKATOLE, $C_6H_4<\substack{-NH-\\C(CH_3)}>CH$, is formed during the putrefaction of protein or by fusing the latter with KOH, and is hence found in the fæces; it is found in the African *Viverra civetta*. It forms white scales, m.pt. 95°, with an intense fecal odour.

INDOLE, $C_6H_4<\substack{NH\\CH}>CH$, is of importance owing to its intimate connection with indigo. By treating o-nitrobenzoyl chloride with AgCN, the nitrile is obtained and this, on hydrolysis, gives o-nitrobenzoylformic acid:

$$C_6H_4<\substack{COCl\ (1)\\NO_2\ (2)} \longrightarrow C_6H_4<\substack{CO\cdot CN\\NO_2} \longrightarrow C_6H_4<\substack{CO\cdot COOH\\NO_2};$$

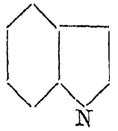
this acid, on reduction, gives the amine, which loses 1 mol. H_2O, forming **Isatin** :

$$C_6H_4\left\langle\begin{matrix}CO\cdot COOH\\ \\NH_2\end{matrix}\right. = H_2O + C_6H_4\left\langle\begin{matrix}CO\\ \\N\end{matrix}\right\rangle C\cdot OH.$$

Isatin

Indole is obtained by distilling oxindole with zinc dust and by various synthetical processes (*see later*, Indigo) ; it is formed in the pancreatic putrefaction of protein or on fusion of this with KOH. In the impure state it has a fecal odour, but when pure and highly diluted it smells like flowers, and is hence used in perfumery. It forms shining scales which melt at 52°, are volatile in steam, and with ozone give indigo.

With sodium bisulphite it forms a crystalline compound, and with nitrous acid a red precipitate ; it imparts a red colour to a pine shaving moistened with HCl. It may be regarded as formed by the condensation of 1 mol. of benzene and 1 mol. of pyrrole :



. It forms numerous derivatives with substituents in the benzene or pyrrole nucleus, the two CH groups near the NH being termed α and β.

INDAZOLE, $C_6H_4\left\langle\begin{matrix}NH\\ \\CH\end{matrix}\right\rangle N$, is a weak base prepared by decomposing the diazo-compound of p-nitro-o-toluidine with acetic acid in the hot and then eliminating the NO_2 group.

INDIGO, $C_{16}H_{10}O_2N$, is a very stable, natural, blue colouring-matter, which was in use in the Far East in the most remote times, and was bartered to the Egyptians—mummies of the Eighteenth Dynasty (1580 years B.C.) are found with wrappings coloured with indigo—then to Greece, and later to Italy. Until the middle of the nineteenth century the trade in indigo remained a monopoly of the Dutch.

FIG. 421.

It is extracted from the branches and leaves (of a yellowish green colour) of *Indigofera tinctoria* (Fig. 421), which grows very readily in tropical countries and is extensively cultivated in India, Java, China, &c., being sown in the spring and cut two or three times a year before flowering.[1] At one time it was extracted also in Europe (Hungary, Thuringia, &c.) from *woad* (*Isatis tinctoria*, Fig. 422), where, however, it occurs only in the leaves and in smaller quantity. There are several varieties of *Indigofera* (tinctoria, disperma, anil,

[1] Indigo belongs to the leguminous plants, and is hence capable of enriching the soil with nitrogenous products owing to the action of bacteria which fix atmospheric nitrogen (*see* vol. i, p. 301). It has therefore been proposed to plant indigo in rotation with sugar-cane, especially in soils which have been exhausted by the latter. At every cutting 25 to 30 quintals of indigo plants are obtainable per hectare and 5 to 6 kilos of 60 per cent. indigo for every ton of plants.

In India indigo is sown in February or March in well-tilled land at the rate of about 14 kilos of seed per hectare. After three months the flowering stage is reached, the plants, which then contain the maximum of colouring-matter, being cut off close to the ground, tied in bundles, and despatched immediately to the factory to be extracted. A second cutting in September gives a smaller quantity of indigo.

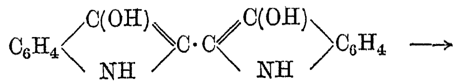
The cultivation of indigo reached its greatest extent in 1896–1897 with a total area of 640,000 hectares, one-third in Bengal, one-fourth in the North-West Provinces, one-fourth in Madras, and one-twelfth in the Punjab. In 1880 India contained 2800 indigo factories and 6000 works employing primitive methods of extraction, the total number of persons employed, exclusive of agricultural labourers, being 360,000. After the appearance of artificial indigo, the area under indigo steadily diminished, being only 180,000 hectares in 1906–1907.

There is a tendency in India to extend the cultivation only on the most suitable soils, and to abandon those less fitted, and in 1908–1909 the area under indigo fell to 115,000 hectares ; in 1909–1910 there was a slight increase to 117,450 hectares.

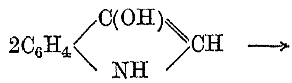
argentea, and others of less importance). They are herbaceous shrubs 50 to 100 cm. in height, covered with silky hairs, with pinnate leaves and many small leaves.

From the results of tests made at Calcutta it would seem that *Indigofera leptostachya*, cultivated in Java but indigenous to Natal, is better in every respect than *Indigofera tinctoria*, while it lasts four to five years. Still better results seem to be given by *Indigofera erecta*.

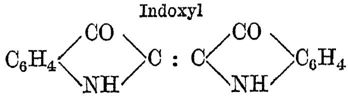
In order that the indigo may be extracted from the cut plants, it is necessary that the glucoside they contain (*indican*)—consisting of a compound of glucose with indigotin (the leuco-base of indigo)—be decomposed by fermentation in large vessels with water. After 10 to 14 hours the glucose is fermented, while the indigo, owing to the presence of ammonia, forms a yellowish solution. The liquid is transferred to deep vats, where it is subjected to "beating" for 2 to 3 hours with wooden paddles or wheels, or to "blowing" by means of a current of air. The oxidation thus effected causes the separation of the indigo in flocks, which are removed by decantation after 3 to 4 hours:



Indigotin



Indoxyl



Indigo blue

FIG. 422.

The 5 per cent. indigo paste separated by decantation is passed through sieves to remove fragments of the plants and is then boiled by means of steam for 15 minutes in order to sterilise the mass—which would otherwise undergo change—and to eliminate part of the brown matter and to effect better separation of the particles of indigo. These then deposit more easily and are collected on a large cloth filter, the first liquid passing through being returned to the filter until it comes through faint red; the 8 to 12 per cent. paste thus obtained is pressed in primitive presses. The large cakes thus formed contain about 80 per cent. of water and are cut into small cubes, which are arranged on grids, dried in the air for two or three months and placed on the market in boxes holding 50 to 140 kilos under the name of *cakes*. During the drying, these cakes evolve ammonia and become covered with mould, which is finally removed with brushes. The yield of indigo is about 0·2 per cent. on the weight of the green plant or 2 per cent. on that of the dry plant.

To combat the competition of artificial indigo, various improvements have been introduced during recent years into the methods of cultivation, manuring, and extraction; attention may be directed to the rational fermentation with suitable enzymes (oxydases) proposed by Calmette and others (Fr. Pats. 300,826 and 302,169).

The indigo-content of the cakes varies considerably, some of those on the market containing only 20 per cent. and others as much as 90 per cent. It hence becomes necessary to determine the value of any sample on the basis of the proportion of pure indigo ascertained by exact analysis.[1] According to Fr. Pat. 323,036 an increased yield and an

[1] **Analysis of Commercial Indigo.** Commercial indigo from Bengal contains, on an average, 60 per cent. of indigotin; that of Madras, 30 to 50 per cent.; that of Java, 72 to 82 per cent.; that of Guatemala, about 40 per cent.; that of Martinique, 60 to 70 per cent.; and that of Cambay, China, and Tonkin, 8 to 15 per cent.

Indigotin can be estimated as follows: 1 grm. of well-dried indigo is mixed (in a bottle with a ground stopper) with 10 grms. of garnets or glass beads and 20 c.c. of sulphuric acid mixture (composed of 3 parts of concentrated sulphuric acid and 1 part of *oleum* containing 20 per cent. of free SO_3). The mass is thoroughly mixed and is afterwards shaken occasionally over a period of 12 hours or so, until solution is complete, the whole being then poured carefully into cold water and the bottle thoroughly rinsed out. The aqueous solution is boiled for 10 minutes and filtered, the filter being washed with hot water until the washings become colourless and the filtrate then made

improved product are obtained by macerating the fresh plants in presence of tannin materials which leave only the indigo undissolved.

The cakes of indigo are blackish blue in colour and give a fracture showing a bronzy reflection. Natural indigo always contains, besides indigotin, other substances and colouring-matters (such as indigo gum, indigo brown and red, &c.) which affect the tint, sometimes favourably.

A good Bengal indigo gave, on analysis, 62 per cent. of indigo blue, 7·3 per cent. of indigo red, 4·7 per cent. of indigo brown, 1·5 per cent. of indigo gum, 6 per cent. of water, and 19 per cent. of mineral matter.

Pure or refined indigo is obtained in various ways, *e.g.* the crude indigo is treated with a mixture of concentrated acetic and sulphuric acids, the indigo alone passing into solution as sulphate, which is decomposed after filtration by excess of water, this precipitating pure indigo or indigotin. In order to avoid dilution with water and loss of acid, it has been proposed to separate the sulphuric acid directly by addition of calcined sodium sulphate, which transforms it into bisulphate ; the acetic acid is then distilled off and the bisulphate removed together with a little water. According to Ger. Pat. 134,139 pure indigo is extracted from the crude product by means of hot, crude pyridine. To purify artificial indigo, it is heated, according to Ger. Pat. 179,351, at 200° to 270°, at which temperature it does not sublime or decompose, while the indigo red and other impurities are destroyed, leaving an indigo highly valued for its fine bronzing.

Of some interest is *colloidal indigo*, which behaves like dissolved indigo, and has been recently prepared by Möhlau by heating, out of contact with the air, a suspension of indigo in an aqueous solution of alkali and sodium hydrosulphite, the liquid being treated, after cooling, with *protalbinic acid* (obtained by Möhlau by the alkaline hydrolysis of protein and subsequent dialysis ; this acid has the power of precipitating various metals in a colloidal state from their salts). Addition of hydrogen peroxide to the filtered liquid gives indigo blue in the colloidal condition, which is retained even after evaporation.

Properties. Pure indigo forms a dark blue powder which, when rubbed, gives a metallic, coppery reflection. It sublimes at about 170°, giving red vapour and forming copper-red, shining prisms. It is insoluble in water, alcohol, ether, alkali, or acid, and dissolves only slightly, even in the hot, in amyl alcohol, chloroform, phenol, carbon disulphide, pure acetic acid, nitrobenzene, aniline or melted paraffin. It has neither odour nor taste and is indeed an almost completely indifferent substance ; this explains why, although materials have been dyed from time immemorial in the Far East, in Europe no process for dyeing textile fibres was discovered for so many centuries—until the sixteenth.

The portion soluble in hot aniline colours this blue but colours fused paraffin purple-red ; from these solutions, rhombic crystals showing marked dichroism separate on cooling.

From hot oil of turpentine indigo crystallises in blue plates.

Concentrated sulphuric acid converts it in the hot into a monosulphonic derivative, soluble in water but insoluble in salt solutions. With fuming sulphuric acid it forms the disulphonic compound, which gives more soluble salts, the sodium salt being sold as a paste under the name of *indigo-carmine*, this dyeing wool like an acid aniline dye.

When dry distilled, indigo gives aniline and other aromatic compounds.

up to a litre. Fifty cubic centimetres of this solution are mixed with 900 c.c. of distilled water, and the liquid titrated with 0·05 per cent. potassium permanganate solution until the blue colour becomes golden yellow without green reflection. In order to accustom the eye to this end-point, which is not sharp, it is advisable to make a comparative test with pure indigo of known strength ; 1 c.c. of the permanganate solution corresponds with about 0 00125 grm. of indigotin. In order to prepare pure 100 per cent. indigo for purposes of comparison, 10 grms. of pure, powdered artificial indigo (98 per cent.) marked B.A.S.F. or M.L.B.) are treated in a beaker with 120 grms. of caustic soda solution (sp. gr. 1·21), 330 grms. of concentrated sodium hydrosulphite solution and 100 grms. of water (or, if 50 grms. of 20 per cent. indigo paste are taken, only 60 grms. of water are added), the mixture being heated on a water-bath at 40° to 50° with occasional shaking and the air being gradually expelled from the beaker by means of a current of coal-gas. When solution is complete, the liquid is rapidly filtered and a current of air passed into the yellow or greenish filtrate. The precipitated indigo is collected on a hardened filter and washed first with hot water, then with hot dilute hydrochloric acid (30 c.c. of the concentrated acid diluted to a litre), next with water again, and repeatedly with alcohol and with alcohol and ether. When dried at 101° to 110° until of constant weight, the product represents pure 100 per cent. indigo.

Energetic oxidising agents (nitric or chromic acid or permanganate) decolorise it more or less rapidly, converting it into isatin. Chlorine, bromine, and iodine give halogenated derivatives of isatin.

The *white indigotin*, which is the leuco-base of indigo blue, is obtained from the latter in a soluble form, by the action of alkaline reducing agents (sodium amalgam, ferrous sulphate, hypophosphorous or hydrosulphurous acid, glucose, gallic acid, &c.) or enzymes. When heated with acid, the greenish yellow alkaline solution deposits indigotin white, which is readily converted into the blue form by the oxygen of the air.

Indigo may be regarded as a substantive dye which colours both animal and vegetable fibres without a mordant. It is first reduced in the vats by means of enzymes in presence of sugar, urine, zinc, arsenic, or reducing salts (sulphites, hydrosulphites), thus becoming decolorised, soluble in alkali and capable of impregnating textile fibres, on which it becomes firmly fixed when rendered insoluble by the action of atmospheric oxygen.

In 1890 the German Government permitted alizarin blue to be used for dyeing part of the cloth for military uniforms, these having been previously coloured exclusively with indigo.

The first efforts to ascertain the chemical nature of indigo were those of Erdmann and of Laurent, who simultaneously (in 1841) obtained isatin by oxidising indigo with nitric acid. In 1848 Fritzsche obtained aniline by distilling indigo with caustic potash; Baeyer and Knop, in 1865, reduced indigo to dioxyindole, oxindole, and indole, the last of these being prepared synthetically by Baeyer and Emmerling in 1869 from o-nitrocinnamic acid. In 1870 Engler and Emmerling effected the first complete synthesis of indigo by heating o-nitroacetophenone with lime and zinc dust, and in 1874 Nencki prepared indigo by oxidising indole with ozone.

In an interesting series of studies extending from 1870 to 1878 Baeyer and his pupils established the constitution of, and synthesised, *oxindole*, transforming it into isatin, and the latter, in various ways, into indigo. The new complete synthesis effected by Baeyer in 1880–1882 firmly established the structure of the indigo molecule.

Of the new syntheses of indigo following that of Baeyer—which, in spite of costly attempts, could not be rendered capable of industrial application—the most important from a practical point of view is that of Heumann (1890), in which fusion of phenylglycine-o-carboxylic acid with alkali is succeeded by oxidation.

The starting-point and the various intermediate products of Baeyer's 1880 synthesis of indigo are as follow:

$$C_6H_4<\substack{CH_2\cdot CO_2H\\ NO_2} \longrightarrow C_6H_4<\substack{CH_2\\ NH}>CO \longrightarrow C_6H_4<\substack{C(:NOH)\\ NH}>CO \longrightarrow$$

o-Nitrophenylacetic acid — Oxindole — Isatoxime

$$C_6H_4<\substack{CH(NH_2)\\ NH}>CO \longrightarrow C_6H_4<\substack{CO\\ NH}>CO \longrightarrow C_6H_4<\substack{CO\\ NH}>CCl_2 \longrightarrow$$

Amino-oxindole — Isatin — Isatin chloride

$$C_6H_4<\substack{CO\\ NH}>C : C<\substack{CO\\ NH}>C_6H_4$$

Indigo

Baeyer's other synthesis, which was tried on an industrial scale by the Badische Anilin- und Soda-Fabrik of Ludwigshafen in 1882, and gave a yield of 60 per cent., started from benzaldehyde, the product of the interaction of benzylidene chloride and sodium acetate being nitrated (and subsequently esterified) and a mixture of 70 per cent. of o-nitrocinnamic acid and 30 per cent. of p-nitrocinnamic acid thus obtained. After removal of the latter, the former is converted into the dibromide, which, with alcoholic potash, loses 2HBr and forms o-nitrophenylpropiolic acid, this giving indigo when heated with alkali and glucose:

$$C_6H_4<\substack{CH : CH\cdot CO_2H\\ NO_2} \longrightarrow C_6H_4<\substack{C : C\cdot CO_2H\\ NO_2} \longrightarrow C_6H_4<\substack{CO\\ NH}>C : C<\substack{CO\\ NH}>C_6H_4$$

o-Nitrocinnamic acid — o-Nitrophenylpropiolic acid — Indigo

Owing to the high price of o-nitrophenylpropiolic acid, this artificial indigo is used only for printing textiles.

In 1882, by means of a new and theoretically elegant synthesis, Baeyer and Drewsen succeeded in raising the yield to 70 per cent.; o-nitrobenzaldehyde and acetone were condensed in presence of caustic soda, indigo being formed as follows:

$$2C_6H_4\genfrac{<}{}{0pt}{}{CHO}{NO_2} + 2CH_3\cdot CO\cdot CH_3 = 2C_6H_4\genfrac{<}{}{0pt}{}{CH(OH)\cdot CH_2\cdot CO\cdot CH_3}{NO_2} =$$

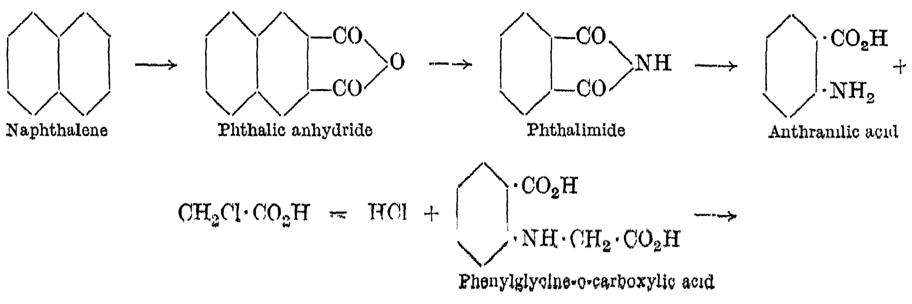
o-Nitrobenzaldehyde   Acetone

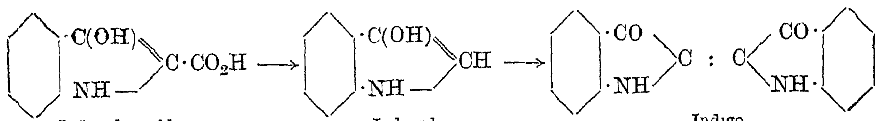
$$2H_2O + 2CH_3\cdot CO_2H + C_6H_4\genfrac{<}{>}{0pt}{}{CO}{NH}C : C\genfrac{<}{>}{0pt}{}{CO}{NH}C_6H_4$$

Indigo

In printing, the synthesis takes place directly on the textile, the acetone being rendered soluble by conversion into the bisulphite compound (*Kalle's salt*). The industrial preparation of o-nitrobenzaldehyde presented, however, a serious disadvantage, the direct nitration of benzaldehyde yielding a considerable proportion of the unusable m-nitrobenzaldehyde; while, starting from benzil, the p-nitro-compound is obtained. A happy solution of this difficulty was found in the preparation of o-nitrotoluene directly from toluene (only 40 per cent. of p-nitrotoluene is formed), oxidation with manganese dioxide and sulphuric acid then giving a good yield of o-nitrobenzaldehyde. To the general application of this process were opposed a number of difficulties. In order that the artificial indigo might displace the natural product, the annual consumption of which was about 5,000,000 to 6,000,000 of kilos (100 per cent.), it was necessary that there should be on the market a sufficient quantity of raw material (toluene) at a reasonable price. It was found that, even although the use of modern metallurgical coke furnaces (*see* vol. i, p. 366, and this vol., p. 530) increased the quantity of crude benzene (in 1900 the total output in Europe amounted to 30,000 tons), yet, since the latter contains only one-sixth of its weight of toluene and since 4 kilos of toluene are required to furnish 1 kilo of artificial indigo, the use of all the toluene extractable from the benzene on the market would give only 1,000,000 kilos of indigo, *i.e.* one-fifth or one-sixth of the whole consumption. Increase of the production of crude benzene for the purpose of obtaining more toluene would lead to over-production of unusable benzene, and hence to increase in the price of toluene and hence in that of artificial indigo, which would be unable to compete with the natural product.

After much further investigation and many unsuccessful trials, the industrial preparation of artificial indigo has, however, become an accomplished fact. Having acquired Baeyer's patents for a sum approaching £20,000 without deriving any practical benefit from them, the Badische Anilin- und Soda-Fabrik of Ludwigshafen did not hesitate to purchase later the patents of K. Heumann, who was the first to discover, in 1890, that indigo is obtained on fusion of phenylglycocoll with caustic potash, but that a better yield is obtained if the phenylglycocoll is replaced by phenylglycine-o-carboxylic acid, $C_6H_4(CO_2H)(NH\cdot CH_2\cdot CO_2H)$. The economical preparation of this acid necessitated investigations and trials extending over more than seven years, and the synthesis became of industrial value only when it was found possible to employ naphthalene as the initial substance. Quite 50,000 tons of naphthalene are produced annually in the distillation of tar, and up to that time only about 15,000 tons of this had been utilised, the rest being left in the heavy tar-oils or used for making lamp-black (p. 528). The complete synthesis takes place in the following stages:




Indoxylic acid — Indoxyl — Indigo

The oxidation of naphthalene to phthalic anhydride by means of chromic acid is too expensive, but the same end was attained by the use of fuming sulphuric acid rich in sulphur trioxide, after it had become possible to prepare this cheaply by the catalytic method (*see* vol. i). The action of the acid was moderated with mercury bisulphate, while the sulphur dioxide was recovered by the catalytic process (in 1901 the Badische Company recovered in this way, for the manufacture of phthalic anhydride alone, about 40,000 tons of sulphur dioxide).

Phthalimide is then easily obtained by the action of ammonia, while the monochloroacetic acid can be prepared cheaply and in large quantity by using the liquid chlorine (1,000,000 kilos in 1900) resulting from the electrolytic manufacture of caustic soda or potash and glacial acetic acid (about 20,000 quintals obtained per annum from the distillation of 100,000 cu. metres of wood). The reaction between anthranilic acid and monochloroacetic acid proceeds readily, but the formation of indoxylic acid was found to be much more difficult, the conditions required for the fusion of the phenylglycinecarboxylic acid being inconvenient; this obstacle was, however, finally overcome. The ultimate oxidation of the indoxyl is effected by means of a current of air. The indigo separates in small crystals, and in order to obtain it in a finely divided state, it is converted into sulphate and this decomposed with water. After being washed, the paste thus formed is identical with natural indigo and is, indeed, of greater value owing to its higher purity and to its constancy of composition.

Process of the Farbwerke vormals Meister, Lucius und Brüning (*of Höchst*). This consists in the action of sodamide (obtained by treating gaseous ammonia with sodium) on phenylglycocoll, subsequently heating in an autoclave at 250°:

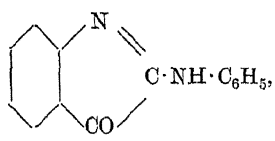
$$NH_2Na + C_6H_5\cdot NH\cdot CH_2\cdot CO_2Na = NH_3 + Na_2O + C_6H_4{<}\substack{CO\\NH}{>}CH_2 \text{ (indoxyl),}$$

2 mols. of the indoxyl then condensing in presence of oxygen:

$$2C_6H_4{<}\substack{CO\\NH}{>}CH_2 + O_2 = 2H_2O + C_6H_4{<}\substack{CO\\NH}{>}C : C{<}\substack{CO\\NH}{>}C_6H_4.$$

This process was originally patented by the Deutsche Gold- und Silber-Scheide Anstalt (Frankfort), from whom it was purchased. A yield as high as 65 per cent. has been obtained, but sodium at 28*d.* per kilo is too expensive to make the process practicable.

Sandmeyer's synthesis (patented by Messrs. Geigy of Basle; Eng. Pat. 15,497 of 1899). Aniline is treated with carbon disulphide in presence of alcoholic potash, diphenylthiourea being obtained: $CS_2 + KOH + 2C_6H_5\cdot NH_2 = KHS + CS(NH\ C_6H_5)_2 + H_2O$. The action of lead cyanide on diphenylthiourea gives **Hydrocyanocarbodiphenylimide**, $\substack{C_6H_5\cdot N\\C_6H_5\cdot NH}{>}C.CN$, which with ammonium sulphide yields the **Thioamide**, $\substack{C_6H_5\cdot N\\C_6H_5\cdot NH}{>}C\cdot C{<}\substack{NH_2\\S}$, and this with sulphuric acid forms α-**Isatinanilide**,



reduction of the latter by means of ammonium sulphide then giving indigo. All the materials used in this synthesis are cheap, but the indigo produced was not able to compete for long with that of the Badische Company and of Messrs. Meister, Lucius und Brüning, who continually lowered the price in order to suppress natural indigo and made use of the two improved Heumann processes starting from phenylglycocoll and phenylglycinecarboxylic acid.

The struggle, lasting for more than twenty years, between the producers of natural indigo and the scientific men connected with the various industrial undertakings has now ended in uncontested victory for the latter. The figures already given showing the areas under indigo at different times (*see* p. 639) justify the conviction that in a few years time *Indigofera tinctoria* will be of interest only historically, just as is the case with madder, now supplanted by artificial alizarin.

With its lower price, its more ready applicability in dyeing, and the considerable use now made of its halogenated derivatives, the consumption of indigo will certainly increase. In 1908, owing to the slight difficulty of reducing indigo, even when finely powdered, several firms placed on the market the leuco-product itself (indigo white), this being obtained by reduction with iron and alkali, or, better, with hydrosulphite (*Grandmougin*), &c.

The following figures will give a clearer idea of the commercial and industrial importance of indigo, both natural and artificial.

Statistics. The production in India was 50,000 quintals in 1892 and 75,000 quintals (containing 56 to 70 per cent. of indigotin), of the value of £3,200,000, in 1896, while in 1909 it was only 12,000 and in 1910 9000 quintals (£240,000). Of Indian indigo 60 per cent. is sold at Calcutta, which supplies Europe and America, 30 per cent. at Madras to Egypt and the East, and 10 per cent. at Bombay and Karachi. In 1882 the Indian Government abolished the export duty on indigo. Until 1865 almost all the indigo was sent to London, which was the centre of the European trade. In 1905–1906 exportation from India had fallen to 15,000 quintals (£400,000), the cultivation of indigo being replaced by that of *rubber* (28,000 quintals), *turmeric* (25,000 quintals), hemp, cotton, tanning plants, &c During recent years the cultivation of natural indigo has increased in the districts more suitable to it and diminished in those less fitted.

The amount of indigo produced in British India in 1911 was 6 per cent. in advance of that of the preceding year, although the area under cultivation was 2 per cent. less.

England imported:

Natural indigo	1909	500 tons of the value of	£139,335
	1910	167 ,, ,, .	43,054
	1911	245 ,, ,, .	67,430
Artificial indigo	1909	1670 ,, ,, .	117,100
	1910	1450 ,, ,, .	101,249
	1911	1215 ,, ,, .	85,143

The United States imported 3100 tons of natural and artificial indigo of the value of £229,800 in 1910 and 3400 tons of the value of £224,600 in 1911.

In 1854 the Philippines exported 194,727 kilos of indigo paste (£17,445) and liquid indigo (*tintarron*) (£5470), while in 1866 the amounts were 251,574 kilos of indigo paste (£96,950) and 959,206 kilos of liquid indigo (£28,180). The industry was still flourishing in 1875–1881, when the producers began to adulterate with sand and other substances; prices were thus ruined and fell from £12 per quintal to £4, the cultivation being to some extent abandoned. With careful cultivation, as much as 4 quintals of good indigo can be obtained per hectare. By 1905 the exportation had diminished to a total of 250,000 kilos of pasty and liquid indigo. The output in Java amounted to 547,000 kilos in 1904 and to 500,000 in 1905, but in 1908 the exports were only 105,000 and in 1909 100,000 kilos.

In 1895 the consumption of indigo in different countries was as follows: England, 13,000 quintals; United States, 11,500; Germany, 10,000; France, 7100; Belgium, 1500; Austro-Hungary, 5500. In 1911 the world's consumption of indigo (calculated for 100 per cent.) was estimated to be about 60,000 quintals, but is possibly higher than this, the amounts used in China and some other countries not being known exactly. In 1900 the Badische Anilin- und Soda-Fabrik produced 10,000 quintals of *artificial indigo*, which corresponds with the output from 104,000 hectares.

Italy imported the following quantities of natural and artificial indigo:

	1903	1906	1907	1908	1909	1910
Natural, quintals . .	5564	1419	972	944	910	474 (£13,270)
Artificial, quintals . .	—	2956	3028	3474	4243	5164 (£72,300)

The quantities of artificial indigo (20 per cent.) exported from Germany in 1900 (and in 1905), in quintals, were as follows: to England 1668 (15,612); to France, 1000 (1350);

to Austria-Hungary, 3773 (11,407); to Russia, 950 (3160); to Italy, 1078 (3200, worth £76,800; besides 2160 quintals of natural indigo of the value of £52,000); to Belgium, 385 (2346); to Switzerland, 595 (819); to the United States, 4926 (25,357); China, 1189 (26,000); and Japan, 174 (7000). In 1907 the *total production of artificial indigo* was about 43,200 quintals (of 100 per cent.), *i.e.* four-fifths of the world's consumption. In the same year Germany exported artificial indigo to the value of £2,000,000 (in 1910 £2,160,000) and imported natural indigo worth £60,000; in 1908 the exports were 154,560 quintals, and in 1910 about 161 quintals.

The price of natural indigo reached its maximum of 22*s.* per kilo in 1870, at which time aniline dyes came into competition with it.

The price of artificial indigo (calculated to 100 per cent.) in 1897 was 15*s.* to 16*s.* per kilo, a corresponding amount of the natural product costing 16*s.* to 18*s.* In 1900 natural indigo cost 12*s.*, while in 1905 artificial indigo was sold at one-half the price of the natural dye, *i.e.* at about 1*s.* 7*d.* per kilo of 20 per cent. strength.

The first artificial indigo plant of the Badische Anilin- und Soda-Fabrik in 1897 cost £480,000, and in 1900 two competitors, namely, Messrs. Meister, Lucius und Brüning and Messrs. Geigy, made their appearance, the considerable fall in price thus produced resulting in Messrs. Geigy's abandonment of the manufacture and of the fusion of the indigo interests of the two remaining firms with a capital of £1,200,000. In 1910 the manufacture of artificial indigo was started by the Rahtjen Company of Hamburg—which is a company with a capital of £280,000 and makes use of Rahtjen's improved Sandmeyer process—and by the firm of Heyden (Radebeuf), which employs the phenylglycine method. The Society of Chemical Industry in Basle also began making artificial indigo in 1911–1912.

R. COLOURING-MATTERS

Only a certain proportion of the innumerable *coloured substances* are capable of being fixed on vegetable or animal fibres, imparting to them a more or less stable coloration, and only those able to fulfil this function, directly or indirectly, belong to the true **Colouring-Matters.**

Coloured substances are those which absorb constituents of white light of certain definite wave-lengths, emitting the rest.

Generally speaking, only the luminous waves visible to the eye have yet been closely studied, and it is probable that new laws, possibly more important than those already known, will be discovered when the infra-red and ultra-violet rays absorbed or reflected by coloured substances are considered.

Hartley has indeed shown that the apparently colourless substance, benzene, is, strictly speaking, coloured, as it absorbs certain ultra-violet rays invisible to the eye, and that in the benzene series the luminous vibrations are gradually rendered slower and so made visible as the molecular weight is increased by substituent groups.

Dichroic Substances allow certain rays to traverse them and reflect certain others, so that they appear to be of one colour by transmitted, and of another by reflected, light; such are, for example, fluorescent substances. Certain alkaline fluorides, such as those of the alkali metals, allow infra-red and ultra-violet radiations to pass through them, while various nitrates, nitric acid, the hydrocarbons, the aldehydes, &c., although they do not retain any of the constituents of white light and hence appear colourless, yet do absorb waves of many wave-lengths.

Light itself is to the human organism only a sensation due to absorption of a portion of the radiations by the crystalline lens of the eye.

Between coloured and non-coloured substances there is often complete or nearly complete identity in chemical *composition*, so that the colour depends, not on the composition, but only on the *constitution* or atomic structure of the molecule.

It is now universally admitted that the colour of substances is closely

dependent on the presence in the molecule of certain well-defined atomic groupings or nuclei.

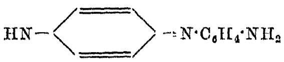
The various organic substances of the benzene series which form coloured or colouring matters always contain these groups (*chromophores, see below*), some of which are univalent and quite simple, *e.g.* $—NO_2$, $X—N=N—$, $X—CO—$. But of more importance are the divalent groups formed of a benzene nucleus of the constitution $>C<\begin{smallmatrix}CH : CH\\ CH : CH\end{smallmatrix}>CX_2$, where X_2 may be O, NH, NR, CR_2, while the other two valencies in the para-position may be satisfied by O, NH, N, R_2, Cl.

As early as 1867 Graebe and Liebermann arrived at the conclusion that the colouring-matters capable of fixing hydrogen with decoloration and formation of the so-called *leuco-bases* (*see* p. 607), are transformed into coloured substances on oxidation.[1]

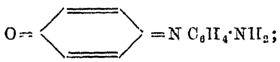
In 1876 N. O. Witt defined the nature of these *simple groups*, which are always contained in the *more complex benzene groups* characteristic of the colouring-matters, terming the former *chromophores* and the latter *chromogens*.[2]

[1] Some of these leuco-products regenerate the original colouring-matter simply by oxidation, while others do not. For instance, reduction of nitro-groups gives, as final products, amino-derivatives, which yield nitro-groups again on oxidation. The complete reduction of azo-compounds yields amino-groups, but there may also be intermediate, less highly reduced products (hydrazo-compounds), which are themselves new *leuco-derivatives*.

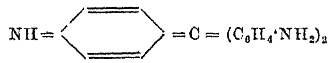
[2] Examples of *chromogens* are :



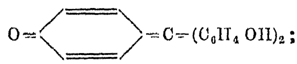
Indamine



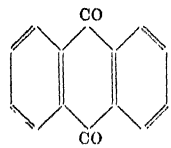
Indophenol



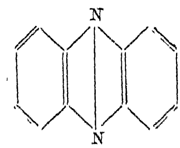
Rosaniline



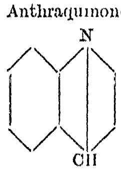
Rosolic acid



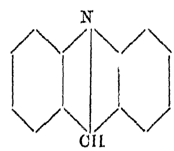
Anthraquinone



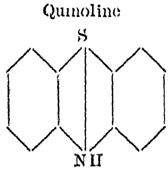
Phenazine



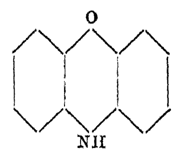
Quinoline



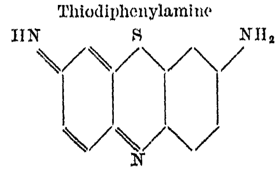
Acridine



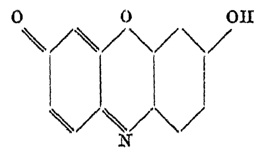
Thiodiphenylamine



Phenoxazine



Thionine



Resorufin

In these chromogens is seen the analogy between the chromophores in the different molecules, characterised by divalent or polyvalent atoms or atomic groups ($=NH$, $=N—$, $=C=O$, S, —O—, $>CO$) united to the ring in a closed chain, the whole forming the true chromophore, which, joined to the rest of the molecule, gives the chromogen.

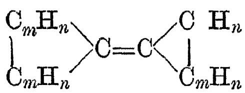
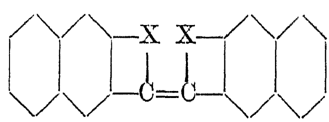
The passage from simple to more complex chromophores is often accompanied by change from a yellow colour to a more intense yellow or to red or blue.

The latter are colourless or slightly coloured but approximate to the colouring-matters in chemical composition. It is, indeed, sufficient to introduce into the chromogen, in place of hydrogen, a salt-forming basic or acid radical (OH, SO_3H, CO_2H, NH_2), to produce the colouring-matter. Thus, nitrobenzene, $C_6H_5 \cdot NO_2$, is a chromogen which becomes a true colouring-matter in nitrophenol, $C_6H_4(OH) \cdot NO_2$, and in nitraniline (phenol itself, $C_6H_5 \cdot OH$, is colourless). The intensity of the coloration increases with the number of these acid or basic groups; thus,

Aminoazobenzene, $C_{12}H_9N_2 \cdot NH_2$, is pale yellow,
Diaminoazobenzene, $C_{12}H_8N_2(NH_2)_2$, is orange, and
Triaminoazobenzene, $C_{12}H_7N_2(NH_2)_3$, is brown.

Such regularities often occur with artificial colouring-matters, so that the colour of a new compound of a certain constitution can be foretold before the compound is prepared.[1]

In the light of the above definition it would be difficult to understand how colouring-matters could be formed of hydrocarbons alone, since these contain none of the characteristic chromophores just mentioned. The few hydrocarbon colouring-matters were for some time regarded as exceptions, but it was found later that they contain a characteristic complex chromophore, different from those previously known and with molecular weight higher than a certain limit. The following two chromophores, for example, are well defined:


and


Further, what are usually the more energetic chromophores cease to be so when they occur in molecules which are small or poor in carbon. To this is due the very small number of colouring-matters in the aliphatic series.

Thirteen chromophores of well-defined constitution are now known, while concerning others there is still doubt owing to the pseudoisomerism (tautomerism) they exhibit.[2]

[1] With fuchsines (rosanilines and p-rosanilines) the colour becomes more intense and more violet with increase in the alkyl groups replacing the aminic hydrogen. The faintly acid, phenolic colouring-matters which are fixed by mordants give highly resistant colours if they contain at least two OH groups, or OH and COOH, in the *ortho*-position, and better still if these are also in ortho-positions with respect to the chromophores. In the colouring-matters of the nitrophenol group, the colour passes from greenish yellow to orange-yellow as the distance between the OH and NO_2 groups increases. Fast colours on mordants are given especially by those colouring-matters containing hydroxyl-groups in the ortho-position with respect to one another and to the chromophore (alizarin, &c.).

Of the triphenylmethane colouring-matters, those which have a sulphonic group (SO_3H) in the ortho-position with respect to the central carbon atom are stable to alkali and to soap (Suais and Sandmeyer).

[2] According to Hantzsch (1906) all the true nitro-hydrocarbons of the aromatic or aliphatic series and also all polynitro-compounds are colourless when quite pure, so that the NO_2 group by itself is never a chromophore. Only certain nitrophenols are coloured when their phenolic hydrogen is free and hence mobile (forming tautomeric compounds) and for the same reason all salts of nitrophenols are coloured. By the discovery of the quinonic (aci-) ethers of nitrophenols besides the true ethers, it was shown that many colourless or almost colourless hydrogenated compounds capable of forming highly hydrogenated salts, are pseudo-acids, so that the coloured salts are derived from a hydrogenated compound differing from the original; if it were possible to obtain these free, they also would be coloured.

Nitrophenols are certainly true tautomeric hydrogenated compounds which give two series of structurally isomeric ethers, such as are given also by nitrous, sulphurous, hydrocyanic, and cyanic acids. The true nitrophenolic ethers are colourless, while the aci-ethers (tautomeric) are coloured an intense red; the former correspond with the general formula, $C_6H_4\begin{cases} O \cdot C_nH_{2n+1} \\ NO_2 \end{cases}$ (derived from the colourless true nitrophenol, $C_6H_4\begin{cases} OH \\ NO_2 \end{cases}$), and the latter with $C_6H_4\begin{cases} O \\ NO \cdot OC_nH_{2n+1} \end{cases}$ [derivatives of aci-nitrophenol (quinonic), $C_6H_4\begin{cases} O \\ NO \cdot OH \end{cases}$]. It is hence possible to tell, from the mere colour, to which of the two groups a given nitro-compound belongs. When true nitrophenols (even in the solid state) are slightly coloured, it is assumed that a minimal quantity of the aci-nitrophenol is dissolved in a large quantity of true nitrophenol (solid solution). Also, the fact that the colour of the substance is sometimes not intensified by increase in the number of nitro-groups is explainable, not on the old view of the theory of chromophores, but only by the new *theory of transposition* (tautomerism):

$$C_6H_4\begin{cases} OH \\ NO_2 \end{cases} \rightleftarrows C_6H_4\begin{cases} O \\ NO \cdot OH \end{cases}$$

In practical dyeing it is of interest to know, not only that a substance has colouring properties but to what chemical conditions or groups these properties are due. Especially is this the case with animal and vegetable textile fibres (*see* Theory of Dyeing, p. 708).

Chromophores are generally of basic (electropositive) or acid character (electro-negative, *e.g.* the *quinonoid group*, &c.) and when they form coloured substances do not retain their colouring properties; the latter are, however, manifested if the basic or acid character is reinforced or even inverted by means of *salt-forming groups*.

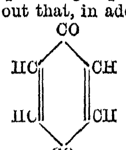
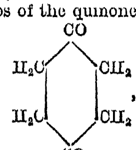
The acid groups (SO_3H, CO_2H, &c.) have, however, a slight influence on the colour. Thus, azobenzene, $C_6H_5 \cdot N : N \cdot C_6H_5$, although a coloured chromogen (containing the chromophore $\cdot N : N \cdot$) does not colour textile fibres since it is neutral, while its sulphonic derivative is a feeble colouring-matter.

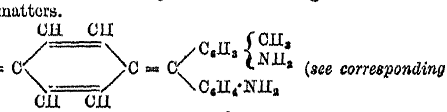
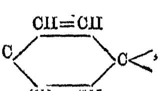
The basic groups (especially NH_2 and, in some cases, OH, &c.), on the other hand, exert considerable influence on the colour, and Witt calls them *auxochrome groups* to distinguish them from the acid groups, which he terms *salt-forming groups*.[1]

The tendency to tautomeric transposition may, indeed, be increased or diminished by the entry of new groups. Thus, in solutions of nitrophenols and their salts, the coloration is not—as it would be according to the modern theory of indicators (*see* vol. i, p. 97)—due to ionisation, but rather to the formation of coloured tautomeric compounds (aci-nitrophenolic ethers) in agreement with the old chemical theory of indicators.

It is thus proved that the formation of coloured salts and coloured ions derived from colourless hydrogenated compounds is of a purely chemical nature. It is caused first of all by intramolecular transposition, from which, by the action of a positive metal (salt), there results a negative quinonic atomic grouping (chromophore), the appearance of coloured ions being a secondary reaction. Hence the actions of chromophore and of auxochrome cannot be held to be distinct but are exerted together, both of them (nitro- and phenol-group) causing the appearance of colour at the expense of their mutual transformation, which generates a quinonic grouping containing neither nitro- nor phenolic group.

These views may be extended to other groups of organic substances since, in general, colourless acids unchangeable in constitution (*i e.* not giving tautomeric forms) give only colourless ions and yield colourless salts with colourless metallic oxides, and colourless ethers and esters with colourless organic radicals (alkyl and acyl). If coloured ions and salts are derived from a colourless alkyl compound, it may be stated with certainty that intramolecular change occurs.

According to E. Fischer and O. Fischer (1900) many colouring-matters derive their properties from the presence in the molecule of quinonoid groups, although A. v. Baeyer (1902–1905) and Hantzsch (1905) showed that the true quinone group does not always cause coloration (*i.e.* is not the chromophore), and Kostanecki and Haller pointed out that, in addition to the two carbonyl groups of the quinone, two ethylene double linkings must be present,  ; in fact, diketohexamethylene, , which has not these double bonds, is completely colourless. As a metaquinone with two ethylene double linkings cannot exist such meta-compounds are incapable of producing colouring-matters.

[1] Rosaniline, HN =  (*see corresponding base*, p. 608), which is coloured contains as chromophore the group HN = , and as auxochromes two amino-groups. When the salt with a single molecule of HCl is obtained and the substance is dyed red, proof is given that the salt is formed with the imino-group of the chromophore, since a red coloration is formed on the fibres. On the other hand, salts of rosaniline with two or three molecules of HCl, which form salts also with the auxochrome amino-groups, are yellow but do not dye textile fibres yellow. It can hence be affirmed that the auxochromes do not unite with the fibres and hence have no action as salt-forming groups but only contribute to increase the basic character of the colouring-matter or even to increase the intensity of the colour; this is clearly shown with safranine (*see later and also above*, Aminoazobenzene). In general, the union of an acid chromophore with a basic auxochrome gives colouring-matters of slight intensity; for instance, the nitroanilines are feeble and the nitrophenols more intense colouring-matters.

The replacement of the hydrogen of the auxochrome OH by a metal increases the power of the auxochrome, while an alkyl or aromatic radical lowers it and an acid radical often annuls it. Substitution of the hydrogen of the auxochrome NH_2 by alkyl radicals raises the colouring power, while two aromatic radicals sometimes lower it considerably, exceptions to this being shown by sulphonal and picryl, $C_6H_2(NO_2)_2$, which cause the NH_2 group to assume an acid character. The *hydrazinic* and *hydroxylaminic* groups also behave as *auxochromes*; thus phenylhydrazine is slightly yellow while aniline is colourless, and nitrophenylhydrazine is more highly coloured than nitroaniline. Anthraquinone (faintly acid chromogen) gives an intensely coloured derivative with hydrazine

The acid or basic character of a colouring-matter decides also its behaviour towards different textile fibres—vegetable and animal—and in general *acid colouring-matters* contain the group SO_3H or COOH, the *feebly acid* ones the group OH, and the *basic* ones the groups NH_2, NHR, NR_2, either as chromophore or as auxochrome.

If the auxochrome of a colouring-matter is weak and the chromophore strong, or *vice versa*, the colouring-matter is generally feeble.

For dyeing purposes the colouring-matters are placed on the market in a state soluble in water, the auxochrome groups being converted where possible into salts (*e.g.* SO_3Na, &c.). When wool (which is both basic and acid in character) is dyed with acid colours, since the basic properties of the wool are usually not sufficiently strong to displace the metal (Na) of the acid colour, an energetic acid (acetic or sulphuric) is added to the hot aqueous dyeing bath, this liberating the acid residue of the colouring-matter, which can then combine with the basic group of the wool to form a coloured stable insoluble salt in the fibre itself.

Thus wool is dyed directly both by acid and by basic colours (with the latter it is not necessary to render the bath acid). Cotton, on the other hand, is not usually dyed by acid dyes but only by basic ones, and then only when the fibres are previously mordanted with tannin materials and metallic salts.

During the past twenty years, however, numerous *neutral* or *substantive dyestuffs* have been discovered, capable of dyeing cotton directly in a neutral or faintly alkaline, but not acid, bath, previous mordanting being unnecessary. Many of these colouring-matters have a common *benzidine* group (*see* p. 605), others contain a basic group (primulin) and others again a phenolic group (curcumin). Colouring-matters sometimes acquire this property by mere accumulation of chromophores in a single molecule (Rupe, 1901). The nature of the metal present in these colouring-matters alters to some extent the properties and the affinity towards cotton, but this is always related to the capillary constant of the aqueous solution. The precipitation of the unaltered colouring-matter on the fibres is facilitated by increasing the osmotic pressure of the bath by the addition of considerable quantities of salts (NaCl or Na_2SO_4).

As a rule phenolic compounds form weak colouring-matters, but they have the property of giving intensely coloured *lakes* with metals (phenoxides), the metallic atom united to the phenolic oxygen functioning as an energetic auxochrome. These colouring-matters having no affinity for textile fibres, the latter are previously charged with metallic oxides (*mordants*). Lakes of different colours are formed with different metals (Hummel hence called such colouring-matters *polygenetic*), but for practical purposes it is indispensable that they should be resistant to atmospheric agents and to ordinary physico-chemical treatment.[1] The best among these substances are those containing in the ortho-position either two phenolic groups (OH) or one OH and one COOH, and of such those are best in which these groups are in the ortho-position with respect to the chromophore (Liebermann and Kostanecki,

groups. The hydroxylamine derivatives are few in number and have been but little studied. H. Kaufmann (1911) has shown that two auxochromes reinforce one another when they are in the para-position and to a less extent or not at all when they are in the ortho- or meta-position. This rule is confirmed, not only by the greater intensity of the colour, but also by the increased luminescence or fluorescence assumed by these substances when they are exposed to ultra-violet rays (*see* vol. i, p. 121); in solution, only compounds of the para- series give direct fluorescence. By the law of distribution it is proved that the maximum and sometimes the only effect of auxochromes in the para-position is exerted when the chromophore and auxochrome are in the same benzene nucleus.

[1] In addition to what has been already stated with reference to the application of lakes, it may be said that they are derived from acid or basic colouring-matters, coloured pigments or colouring-matters of the anthraquinone group. The soluble acid colouring-matters are precipitated by salts of calcium, barium, strontium, aluminium (chlorides), magnesium (sulphate), &c. Solutions of basic dyes are precipitated by tannin, Turkey red oil, resin, or, more commonly, sodium phosphate or sodium arsenate. Anthraquinone dyes (alizarin, cœrulein, &c.) form lakes with greater difficulty, and it is necessary to observe rigorously the proper temperature conditions. In preparing lakes, great importance attaches also to the substance on which the precipitated lake is deposited or with which it is mixed (aluminium hydroxide, barytes, zinc or lead white, ferric oxide, fresh aluminium silicate, &c.), and of these, the ones more easily decomposable by dilute acids retain the colour best. Lake-formation is hence not a simple absorption phenomenon but also a chemical phenomenon.

1887–1893) and in which the auxochrome is formed from iron, aluminium, or chromium. Not all colouring-matters which give insoluble lakes can be fixed on fibres mordanted with metallic oxides, and this perhaps depends on the fact that only certain coloured lakes are capable of combining with the fibre, the constitution of the colouring-matter (*see* Alizarin) being here also of considerable importance.

When basic or neutral colouring-matters are sulphonated with concentrated H_2SO_4, *acid colouring-matters* (Simpson and Nicholson, 1862) are often obtained. In the form of soluble salts of the alkali metals, these can be fixed directly, in an acid bath, on animal fibres with the same colour as the colouring-matter, the animal fibre forming a kind of new salt; indeed the fibre assumes the colour of the original salt of the colouring-matter and never that of its free coloured acid liberated in the bath by means of acetic or sulphuric acid (*see above*, Process of Dyeing). These acid colours are fixed also by cotton, provided the latter is first rendered basic either by nitrating and then reducing, or by oxidising (oxycellulose), or by hydrating (with NaOH: mercerisation), or by treating with NH_3 under pressure in presence of $ZnCl_2$ (Vignon).

Basic colouring-matters which owe their basicity to the chromophore and more especially to the auxochrome NH_2, form salts with acids and are used in practice in the form of hydrochlorides, sulphates, &c., from hot acidified aqueous solutions of which wool and silk fix the coloured base. These basic dyes also form insoluble salts with tannin, &c., so that they are capable of dyeing cotton —which has no affinity for basic dyes—if this is previously mordanted by prolonged immersion in cold solutions of tannin extracts (sumac, &c.), followed by fixation of the tannin in another bath containing an antimony, aluminium or iron salt, or gelatine. In the subsequent dyeing-bath, the dye is fixed rapidly, even in the cold (the fixation is more regular, *i.e.* slower, in presence of a little alum). The full (intense), bright colours thus obtained on cotton resist the different reagents well but are destroyed during washing by the rubbing. In 1901 C. Favre suggested the use of resorcinol and formaldehyde as mordants in place of tannin.[1] Many colouring-matters exert a poisonous

[1] **Behaviour of Colouring-Matters towards different Fibres and Mordants, according to Noelting.** If a skein of wool, silk, or cotton is immersed for some hours in a solution of a basic ferric salt, the fibres assume a brown colour, having fixed a certain amount of ferric oxide or basic salt. The same holds generally for all salts of oxides corresponding with the formula R_2O_3. The salts of protoxides (RO), *e.g.* those of copper, iron, manganese, nickel, cobalt, &c., especially the tartrates or in presence of tartar, are fixed by wool or silk, but not at all or but slightly by vegetable fibres.

Not only metallic salts, but also certain organic substances (tannin materials) and salts of hydroxyoleic and hydroxystearic (sulpho-oleates) acids, can be fixed by fibres.

A large number of colouring-matters are fixed directly on animal fibres in a neutral or acid bath, more rarely in an alkaline bath. To this group belong the nitro-derivatives of the phenols and amines: the azo, basic, and acid dyes; basic, acid, or sulphonated derivatives of triphenylmethane; certain phthaleins (fluorescein and eosin); the aminophenazines, safranines, thioindamines, phenoxazine derivatives (gallocyanine and Meldola's blue), phenylacridine complexes (phosphine), quinoline complexes (cyanine, quinoline red, quinophthalone), hydrazides, osazones (tartrazine), ketonimides (auramine) and, among the natural colours, indigo-carmine, berberine, safflower, saffron, archil, and catechu. Almost all of these dyes are fixed in minimal quantity or not at all on vegetable fibres. Those which are fixed by the latter are less numerous and include: a first group of substances which are fixed only with difficulty (better with tannin), *e.g.* certain aminoazo-compounds, phenylene brown, chrysoidine, methylene blue, Victoria blue, safranine; a second group fixed stably and directly and consisting of numerous azo-derivatives of benzidine, tolidine, diaminostilbene, p-phenylenediamine, naphthylenediamine, diaminoazobenzene, diaminoazoxybenzene and its homologues, diaminodiphenylamine, canarine (oxidation product of thiocyanates), and the sulphur dyes of Croissant and Bretonnière; a third group which do not dye wool, cotton, or silk directly but give bright fast colours if these fibres (especially with wool) are previously mordanted with salts of iron, aluminium, or chromium: such are certain phthaleins (gallein), derivatives of anthraquinone (alizarin, purpurin, alizarin orange, anthragallol), anthraquinoline (alizarin blue), phenoxyanthranol (cœrulein), and almost all the *natural colouring-matters* (logwood, cochineal, quercitron, cudbear, sandalwood, &c.). Noelting gave the name *substantive dyes* to those which dye animal and vegetable fibres directly and that of *adjective dyes* to those which dye the fibres only after mordanting.

Certain dyestuffs are fixed directly by wool and silk and only indirectly by cotton, *i.e.* when the latter has been mordanted. Such are gallocyanine and various carboxylic acids of azo-compounds. In dyeing with *aniline black*, the fibre fixes both the aniline salt and also the oxidising agent, the latter oxidising the aniline on the fibre with formation of an insoluble aniline black. Dyes which are not fixed directly by cotton, dye it only after mordanting with tannin or sulpholeic acids if they are basic in character, or after mordanting with metallic oxides, with or without sulpholeates, if they are acid.

Further, various substantive colouring-matters have the property of fixing others on them; for instance, chrysamine and canarine, which are yellow, fix basic colouring-matters, such as fuchsine forming an orange, malachit-

action on micro-organisms, as they unite with the protoplasm, and even, in dilute solution, cause death (Th. Bokorny, 1906).

In recent years attempts have been made, but without practical success, to utilise the colouring-matters produced by certain *chromogenic bacteria, e.g. B. prodigiosus*).

MANUFACTURE OF COLOURING-MATTERS

Since 1856–1860, when Perkin in England made mauveine and Renard and Frank in France made fuchsine on an industrial scale, scientific progress in colouring-matters has advanced *pari passu* with the industrial development.

In the history of the artificial colouring-matters, side by side with the names of the scientific men, such as Perkin, Williams, A. W. Hofmann, Graebe, Liebermann, Baeyer, Witt, Nietzki, Noelting, Caro, &c., who laid the first stones in this marvellous chemical edifice, are those, not less worthy, of the brilliant and daring industrial workers who, by uninterrupted energy and the application of ingenious processes, carried these theoretical discoveries into the larger field of industry and commerce.[1]

green forming a yellowish green, and methylene blue forming a blue colour. All the benzidine colours have the same property, to which Noelting gives the name *secondary dyeing*, a term applicable also to all dyeing with mordants. Direct dyeing would then be primary dyeing.

In some cases a third colouring-matter can be superposed; for instance, the violet lake of alizarin and iron combines with methyl violet giving a brilliant triple lake. The red lake of alizarin, alumina, and lime, which is not very bright and rather opaque, is rendered brilliant and more fast by the fixation of a sulpholeate, which forms a quadruple lake; finally, this can still fix tin from a soapy solution of tin salt, a new lake with five components being formed.

If a tissue removed from a solution of a basic iron salt, instead of being washed immediately (in which case it becomes yellowish), is treated directly with alkali or soap (or with a solution of a salt the acid residue of which forms an insoluble compound with oxide of iron), it becomes much more intensely coloured and the quantity of iron fixed by the fibres is considerably increased. Oxide of iron can be accumulated on the fibre, not only, as just mentioned, from an alkaline bath, but also by impregnating the fibre itself with ferrous salts of volatile acids, *e.g.* the acetate, and then exposing it in the moist state to the air. The ferrous salt is thus converted into basic ferric salt, this in warm, moist air losing part of its acid and undergoing change into an insoluble, highly basic salt, which is not removed from the fibre even by repeated washing.

In order to help the action of the air and render a larger quantity of basic salt insoluble, the fibre may be passed into a bath of cow-dung or lime and potassium silicate, phosphate, or arsenate. Aluminium salts are similarly rendered insoluble by formation of a basic salt. The basic chromium salt is fixed by a subsequent bath of sodium carbonate or, better still, by impregnating the tissue with a solution of chromium sesquioxide in caustic soda and exposing it to the air, the caustic alkali being thus converted into carbonate, which precipitates the sesquioxide of chromium; instead of exposure to the air, the action of steam may be employed. Chromous oxide is precipitated by simple washing of the impregnated tissue with a tin salt. Sulphoricinate is fixed by solutions of aluminium salts and tannin by solutions of tartar emetic or ferric or aluminium salts.

The action of a chromate bath or catechu is twofold; first, the catechu undergoes oxidation with considerable darkening, and then combination takes place between the oxidation product and the chromium sesquioxide resulting from the reduction of the chromate.

[1] At first France was at the head of the aniline dye industry, with numerous pioneers, such as Verguin, Renard Brothers, Frank, Poirrier, Gumon Marnas and Bonnet, Coupier, Girard and de Laire, Baubigny, Persoz, Bardy, Lauth, Kopp, Rosenstiel, Roussin, &c., but of all these very few have been able to withstand the wonderful organisation of the large German manufacturers. Even England, the cradle of the industry, is now in a position greatly inferior to that of Germany. The six English factories now working employ altogether 35 chemists, while the six largest German firms employ 600, besides 350 engineers and technical directors. From 1886 to 1900, the English firms took out 86 patents, while the six more important German ones took out 948.

The principal English firms to-day producing dyes are: Brooke, Simpson, and Spiller, London; The Clayton Aniline Company, Manchester; Read, Holliday, and Sons, Limited, Huddersfield; and I. Levinstein and Company, Limited, Manchester.

The German firms which enjoy almost a monopoly of the world's trade in aniline colours are: (1) Badische Anilin- und Soda-Fabrik, Ludwigshafen; (2) Farbenfabriken vormals Fr. Bayer und Co., Elberfeld; (3) Farbwerke vormals Meister, Lucius und Bruning, Hochst; (4) Leopold Cassella and Co., Frankfort; (5) Actien-Gesellschaft fur Anilin-Fabrikation, Berlin; (6) Kalle and Co., Biebrich; of less importance are the firms of Oehler in Offenbach, Leonhardt of Mulheim, &c. Firms (1), (2), and (5) work together to regulate the output and trade, and the same is the case with (3), (4), and (6).

In point of magnitude, the German firms are immediately followed by those of German Switzerland (Basle): Gesellschaft fur chemische Industrie, Durand, Huguenin and Co.; Geigy; Kern and Sandoz, &c.

Of the German factories, the Badische Anilin- und Soda-Fabrik alone, with a capital of over £1,400,000, employed in 1908 about 8000 workmen (in 1896 less than 5000 and in 1865, the first year of working, 30), and more than 160 chemists and 75 engineers; for more than twenty years the dividends paid by this company have been about 25 per cent.

The Bayer Company of Elberfeld employs, in its various works, 170 chemists, 35 engineers, and about 6000 workmen. Its principal works were originally at Elberfeld, but the most important of their manufactures—colouring-matters, pharmaceutical and photographic materials—were transferred several years ago to a new factory at Leverkusen, near Cologne, which occupies an area of 529 hectares and finds employment for 4000 workpeople. Some mention may be made here of the conditions under which the operatives work and the benefits they enjoy. Leaving out of account the fact that the average wage of the workmen is more than five shillings per day, the

The dye industry, although not born on German soil, has there reached its greatest development and borne its richest fruit, far in excess of the dreams of its founders. This result has been reached in Germany as a result of various fortunate circumstances.

This industry does not confine itself to the application or development of discoveries made here and there by individual scientific workers, but has made itself a centre of research. The industry has its own laboratories, which have nothing to distinguish them from those of the more important universities and contain hundreds of chemists controlled by renowned directors. By this means it has been possible to accumulate many details of great practical importance, which escaped those prosecuting research in university laboratories. Such rational systematisation of specialised scientific research in a single branch of industry has cost enormous sums, but has, at the same time, borne fabulous fruits. The investigations and discoveries made in these establishments are of great advantage to science itself, opening up new fields of study and completing and generalising rudimentary rules so that they become positive laws.

The prime materials for dyes are the various aromatic hydrocarbons obtained from tar, which may, however, be first transformed into substances more active chemically (phenols, amines, &c.).

The fundamental reactions to which the distillation products (benzenes, phenols, naphthalene, pyridine, &c.) of tar are subjected consist, in general, of

company, starting from the idea that the *employer owes to the employee more than his wages*, has created a number of institutions which now represent a total capital of £600,000 Among these is a library of 12,000 volumes used by 44 per cent. of the workpeople, the books demanded in 1907 consisting of popular works on scientific subjects to the extent of 52 per cent. and of miscellaneous literature to the extent of 48 per cent.; the library committee consists of chemists, engineers, and workmen. Five hundred baths have been built, 150,000 baths being taken annually. There are dormitories with beds at 2½*d*. per night, refectories which supply the three meals of the day to men for a shilling and to boys and girls for 9*d*. There are also free technical schools and schools of art and music. A lying-in hospital (also for wives of workmen not employed in the factory) cost £7200, the annual expenses being £1600. A hall for theatrical performances and conferences, another for lectures, concerts, &c., and a third for conferences of workmen, cost £18,000. There are sickness funds, savings banks, and a life insurance scheme, supported to the extent of two-thirds by the funds of the company; also old-age pensions, and accident funds in addition to the State fund, the company paying for the first three days after the accident (not paid by the insurance companies) and supplementing the legal payment by 50 per cent. The sale of alcoholic drinks—beer included—is forbidden in the refectories, but coffee, tea, milk, &c., are obtainable at very low prices. On all these institutions the Bayer Company spends more than £80,000 and is yet able to pay its shareholders a dividend of 25 to 30 per cent. on a capital of £1,200,000.

The scientific and technical work of the company is indicated in the 4000 patents filed up to the year 1907.

Many of the Russian and French factories are branches of German ones.

In spite of the optimistic views sometimes expressed, it does not seem possible to start an aniline dye factory in Italy, especially as even in England, which is situated far more favourably as regards raw materials and fuel, this industry has not been able to compete seriously with Germany.

Statistics. Germany now supplies six-sevenths of the world's requirements in artificial organic dyes (although importing from Switzerland special dyes to the value of £200,000 to £250,000), and the progress of the industry is clearly shown by the following data concerning the exports:

	1880	1890	1895	1900	1905	1907	1909
Aniline dyes . tons	2,141	7,280	15,789	23,781	36,570	43,716 (£5,600,000)	47,777
Alizarin dyes . ,,	5,588	7,906	8,928	8,591	9,339	10,500 (£1,200,000)	34,784
Indigo . . ,,	497	733	658	1,873	11,165	16,350 (£2,160,000)	£2,000,000

To the total of £8,960,000 (in 1907) must be added £1,200,000 for various crude materials (aniline oil and salts) for the manufacture of dyes abroad.

Switzerland, with six factories in the canton of Basle, has a capital of £560,000 invested in the manufacture of dyes, which occupies 2000 workpeople and exported 60,000 quintals of dyes, of the value of £880,000, in 1906; in 1910 the value of the exports exceeded £1,000,000, although in 1903 it was not more than £680,000.

In 1905 Italy imported 40,820 quintals of aniline dyes in powder and 4300 in paste (excluding indigo and extracts of dye-woods), of a total value of £532,000 (£400,000 from Germany and the rest almost all from Switzerland). In 1900 the value of the imported dyes was about one-third less than the above, while 53,000 quintals were imported in 1908, 61,890 in 1909, and about 53,560, besides 5500 of pasty dyes, in 1910.

Other countries imported from Germany in 1907 the following quantities of aniline dyes, at an average price of £12 to £13 per quintal: England, 9048 tons; United States, 10,670; Austria-Hungary, 2980; France, 1035 Russia, 1269; Japan, 2649; China, 3476; India, 2040; Belgium, 1490; Switzerland, 680.

In 1909 the value of the aniline dyes imported into China was £280,000, that of the natural indigo £28,000, and that of the artificial indigo £520,000.

nitration, *reduction*, *diazotisation*, *sulphonation*, *fusion* with caustic soda, *chlorination*, and *oxidation*.

These reactions lead to intermediate products very near to the true colouring-matters. Thus, nitrobenzene and its homologues yield aniline, toluidine, &c., by simple reduction with iron turnings and hydrochloric acid, and aniline then gives diphenylamine, dimethylaniline, sulphanilic acid, &c.

Oxidation of aniline, toluidine, &c., gives fuchsine, safranine, methyl violet, &c. The nitroanilines serve for the preparation of azo-dyes, while the action of sulphur on amines leads to primuline and the new class of sulphur-dyestuffs.

With another reducing agent (Zn + KOH), nitrobenzene gives other products (hydrazobenzenes, &c.), from which other classes of colouring-matters originate.

A further important reaction consists in the introduction of sulphuric acid residues (**Sulphonic Group**, SO_3H) into benzene nuclei in place of hydrogen or other groups by treatment of benzene derivatives with concentrated sulphuric acid. The resulting sulphonic acids are of great importance and often decide whether a dyestuff is *acid* in character and hence able to dye wool and silk directly in an acid bath, or *neutral* (or almost so) and capable of colouring cotton directly, or still *basic* and able to dye cotton mordanted with tannin or wool and silk directly in a neutral or faintly alkaline bath.

The sulphonic group, in its turn, may be replaced by hydroxyl by fusion of the sulphonic acid with caustic soda, this being a very important reaction, as it allows of the ready preparation of resorcinol and of **Alizarin**. The OH group may also be introduced into the molecule directly by means of the Bohn-Schmidt reaction, which consists in treating various substances in the hot with sulphur trioxide dissolved in concentrated sulphuric acid.

Oxidation is likewise of great value and was first used for preparing fuchsine, safranine, &c. It has now been found that naphthalene can be oxidised with sulphuric acid in presence of mercury, giving phthalic and anthranilic acids at a cost so low as to admit of the competition of artificial **Indigo** with the natural product (*see* p. 643).

The methods of dyeing textile fibres are becoming continually more simple and more certain and capable of giving the most varied colours. Nowadays stable dyes can be produced directly on the cotton fibre in a single operation, starting with simple chemical reagents. The ideal method would be for the manufacturers of chemical products to furnish reagents to the dyer so that the desired colours could be made directly on the tissues.

CLASSIFICATION OF COLOURING-MATTERS

Nietzki divides the artificial organic colouring-matters into the following general groups, with reference especially to their chemical composition :

I. Nitro- colouring-matters. II. Azo- colouring-matters. III. Derivatives of hydrazones and pyrazolones. IV. Hydroxyquinones and quinoneoximes. V. Diphenyl- and triphenyl-methane colouring-matters. VI. Derivatives of quinonimide. VII. Aniline black. VIII. Quinoline and acridine derivatives. IX. Thiazole colouring-matters. X. Oxyketones, xanthones, flavones, and coumarins. XI. Indigo and similar and other natural colouring-matters. XII. Sulphur colouring-matters.

But for practical dyeing, more importance is attached to the division into the following five groups on the basis of the behaviour of the colouring-matters towards different textile fibres, since in practice it is more important to know if a colouring-matter is basic or acid or if it dyes with or without mordant, than to know if it is a nitro-compound, quinone, hydrazone, &c. :

1. *Basic colouring-matters*, which in a neutral bath dye animal and vegetable fibres; the latter should, however, be previously mordanted with tannin.

2. *Acid colouring-matters*, which dye animal fibres in an acid bath.

3. *Adjective or mordant colouring-matters*, which dye fibres mordanted with metallic oxides (of iron, chromium, aluminium, &c.).

4. *Almost neutral or substantive colouring-matters*, which, as alkali salts, dye vegetable textile fibres directly, without mordanting.

5. *Insoluble colouring-matters or pigments* are formed directly on the fibre, *i.e.* are used for vat-dyeing or are developed on the fibre.

I. NITRO- COLOURING-MATTERS. All the nitro-derivatives of the amines and phenols are energetic dyestuffs, those of the phenols especially being markedly acid colouring-matters, since the Chromophore NO_2 reinforces the acid character of the OH group. Even the basic substances may become acid if many NO_2 groups are present. It is particularly the salts of these compounds which are coloured; p-nitrophenol, for example, is colourless while its salts are yellow.

The coloration of the nitrophenols disappears if the phenolic groups are etherified by alkyl groups.

Of the nitrophenols the ortho-products (OH : NO_2 = 1 : 2) are the more important and the more highly coloured. Examples are: Picric Acid (*trinitrophenol*), $C_6H_2(NO_2)_3{\cdot}OH$; Naphthol Yellow S = *dinitronaphtholsulphonic acid*, $C_{10}H_4(NO_2)(NO_2)(OH)(SO_3H)$ (2 : 4 : 1 : 7); Victoria Yellow (or Victoria orange) = *dinitrocresol*, $C_6H_2(OH)(CH_3)(NO_2)_2$.

II. AZO- COLOURING-MATTERS. The azo- colouring-matters, unlike other groups, have retained their original importance, not only as regards the number that can be produced, but especially because the gradations of colour and the stability can be modified at will. Thus, the azo-group includes *substantive dyestuffs*, which dye cotton without a mordant, wool colouring-matters fast to milling and to sulphuring, and stable adjective dyes such as alizarin.

Their basic chromophore is —N=N— and the chromogen, R—N=N—R′, R and R′ being aromatic radicals.

These compounds form the largest and perhaps the most important group of artificial colouring-matters. They are not of themselves (especially in the case of the more simple ones, such as azobenzene) intense dyestuffs, but they become such on the introduction into the benzene nuclei of acid (OH) or basic (NH_2) auxochromes, and with increase of the number of these the intensity increases, passing from yellow to red, to blue or to brown. Blues are obtained with several chromophores —N=N— (di- and tetra-azo-compounds), while naphthalene groups give reds. The higher the molecular weight the more intense becomes the colour.

In certain cases it must be assumed that these auxochromes are united in some way with the chromophore, and, since β-naphthazobenzene no longer exhibits phenolic character, Liebermann attributed to it the structure $C_6H_5{-}NH{-}\underbrace{N - C_{10}H_6}_{O}$, instead of the ordinary constitutional formula $C_6H_5{\cdot}N : N{\cdot}C_{10}H_6{\cdot}OH$.

Certain azo-compounds show behaviour recalling that of quinones and ketones, *e.g.* they combine with sodium bisulphite. In such case, the formula is represented thus: $C_6H_5{\cdot}NH{\cdot}N : C_6H_{10}O$.

Almost all azo-compounds dissolve in concentrated sulphuric acid, giving a characteristic coloration, which, in general, serves for their recognition and distinction from other colouring-matters (*see* Table *given later*).

Substituted azo-compounds are always obtained by coupling a diazo-compound with a phenol or with an amine, and, in the latter case, diazoamino-compounds are formed as intermediate products.

The first azo-dyestuff of industrial importance (triaminoazobenzene) was prepared in 1867 by Caro and Griess, and it was only with the dyes discovered by Witt and Roussin subsequently to 1876 that this group assumed a position of practical importance.

After 1880 azo- colouring-matters again came to the front owing to the preparation of direct dyes for cotton, and later these dyes were produced directly on the cotton fibre new dyeing methods being thus created,

They are prepared industrially by first diazotising the amine, or its sulphonic acid diluted with water, by means of hydrochloric acid and sodium nitrite, the mass being cooled with ice and tested with starch-potassium iodide paper so as to avoid any large excess of nitrite. After diazotisation, the *coupling* is carried out by pouring the whole slowly into an alkaline solution of the phenol, the mass being kept alkaline. The colouring-matter thus formed is separated in an insoluble state on addition of salt and is then filter-pressed. The reaction between the amines and the diazo-compounds is more complex: $R{\cdot}NH_2,HCl(+\frac{1}{2}N_2O_3) \longrightarrow R{\cdot}NCl : N(+R'OH, \text{phenol}) \longrightarrow HCl + R{\cdot}N : N{\cdot}R'{\cdot}OH$. The diazo-group enters in the para-position to H, OH, or NH_2, or if this is occupied, in the ortho-position.

Azo- colouring-matters are so numerous and so varied in constitution and behaviour that they may be divided into several sub-groups.

The **MONOAZO-COMPOUNDS** may be sulphonated (aminoazo-derivatives give basic colouring-matters and the hydroxyazo-derivatives without carboxyl, acid colouring-matters) or not sulphonated (the aminoazo-compounds give basic and acid colouring-matters and the hydroxyazo-compounds basic and adjective colouring-matters). **POLY-AZO-COMPOUNDS** yield substantive and adjective dyestuffs (*i.e.* without benzidine nuclei and then form acid, basic, and mordant colouring-matters). Finally there is the sub-group, the members of which are generated directly on the cotton fibre.

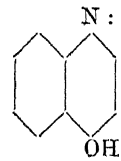
(*a*) **Aminoazo-derivatives.** These are obtained in the usual way, in the cold and in alkaline solution, from diazo-compounds (amino- or not) and amines.

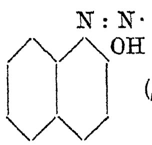
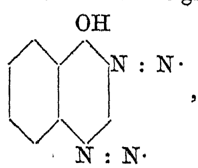
Among these are *fast yellow, acid yellow, tropæolin,* the *oranges, Indian yellow* (*nitro-derivative* of *phenylaminoazobenzenesulphonic acid*), *orange IV* or *tropæolin OO* (sodium salt of the non-nitrated product, $SO_3H{\cdot}C_6H_4\ N : N{\cdot}C_6H_4\ NH{\cdot}C_6H_5$) and *vesuvine* or *Bismarck brown,* which is the hydrochloride of *triaminoazobenzene,* $NH_2{\cdot}C_6H_4{\cdot}N : N{\cdot}C_6H_3(NH_2)_2$, mixed with $C_6H_4[{\cdot}N : N{\cdot}C_6H_3(NH_2)_2]_2$.

Indoin is a basic blue obtained by coupling diazotised safranine with β-naphthol.

On textiles they are not very fast to light, the less fast being those which do not contain the sulphonic group. In printing textiles these colours are corroded by the stannous chloride.

(*b*) **Hydroxyazo-derivatives** (or *azoxy-compounds*), *e.g.* hydroxyazobenzene, $C_6H_5{\cdot}N : N{\cdot}C_6H_4{\cdot}OH$. *Tropæolin O* is a dihydroxyazobenzenesulphonic acid.

Of greatest importance are the derivatives of α- and β-naphthols,  (α)

and  (β), the compounds with the auxochrome in the *ortho* : β-position with respect to the chromophore (·N : N·) being colouring-matters of greater fastness to acid and alkali than the *ortho-* : α-compounds. But if another azo group be introduced into the latter, it will occupy the β-(ortho)-position,  , the fast brown dyestuffs being obtained.

Those most used are the sulphonic derivatives, obtained from various *naphtholsulphonic acids.*

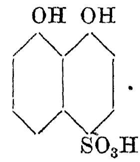
Of the numerous colouring-matters of this group, the most important are: *orange II tropæolin OOO N. II* or *N. I, croceine orange, orange G,* &c., *Ponceau* (various), *Bordeaux S, amaranth, rocelline, croceine, azorubin S* $\left(\begin{array}{l} N{-}C_{10}H_6.SO_3H \quad (4) \\ \| \\ N{-}C_{10}H{<}\begin{array}{l}OH \quad (1)\\ SO_3H \quad (4)\end{array} \end{array}\right)$, &c.

(*c*) **Azo-Colouring-Matters derived from Carboxylic Acids** are obtained from carboxylic diazo-compounds and phenols or amines.

These compounds (especially the o-hydroxycarboxylic acids, such as salicylic acid) have an affinity for metallic mordants, particularly for chromium oxide. The hydroxyl and carboxyl groups are in the ortho-positions.

Among the nitrobenzeneazosulphonic acids are *alizarin yellow*, the *diamond yellows*, &c., which, on cotton and wool, give colours very resistant to light and to fulling. The hydroxyazo-acids include various tropæolins (V, R, O, OOO, &c.), *chrysoin*, *cochineal scarlet*, *ponceau*, *palatine scarlet*, &c.

(*d*) **Azo-Colouring-Matters derived from Dihydroxynaphthalenes.** Several of these compounds are fixed by mordants when they have two hydroxyl groups in the ortho- (1 :) 2 or peri- (1 : 8) position, as in anthraquinone (*see* Alizarin) and



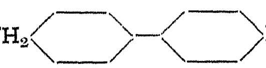
. But these compounds are used practically, not on mordants, but for the dyeing of wool, as they give very regular results (such are the *azofuchsines*), while the peridihydroxynaphthalenes are used on mordants and form the so-called *chromotrop* colouring-matters, which dye unmordanted wool in an acid bath, giving a fine red turned violet by addition of alumina mordants or blue-black with chrome mordants.

POLYAZO-COLOURING-MATTERS (di- and tetra-azo) contain the chromophore ·N : N· several times and vary according as the chromophores are in the same benzene nucleus or in different nuclei and as the auxochromes are or are not in the same nuclei as the chromophores.

Here are found benzidine derivatives in which the two chromophores are in two different nuclei, joined by a single linking.

Among the sulphonic derivatives are, for example, *Biebrich scarlet*, and the croceines, while among the polyazo-compounds are also *naphthol black*, *naphthylamine black D*, *diamond black* (which is obtained from aminosalicylic acid and is fixed by mordants), &c.

BENZIDINE, NH_2



NH_2, when treated with nitrous acid, gives a tetrazo-derivative which yields yellow, red, blue, or violet colours on combination with amines or phenols. With naphthionic acid, tetrazodiphenyl gives *Congo red*, which was the first substantive dyestuff obtained and was patented by C. Böttiger in 1884 :

$$\begin{array}{l} C_6H_4\cdot N : N\cdot C_{10}H_5<\begin{matrix}SO_3H\ (a)\\ NH_2\ \ (a)\end{matrix} \\ | \\ C_6H_4\cdot N : N\cdot C_{10}H_5<\begin{matrix}SO_3H\ (a)\\ NH_2\ \ (a)\end{matrix} \end{array};$$

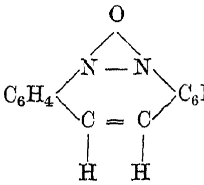
the free sulphonic acid is blue while the salts are red and are fixed *directly on cotton*, but have the disadvantage of becoming blue or black in contact with even weak acids.

The **Benzopurpurins** (*see* p. 605) are obtained in a similar manner.

These benzidine derivatives cease to form substantive colouring-matters if the meta-positions (with respect to the NH_2) are occupied.

Substantive or direct colours, when fixed on cotton, function as weak mordants for basic dyestuffs.

The different firms making colouring-matters place on the market a large number of substantive dyes under various names. For instance, Messrs. Casella have a long and important series of *diamine colours* (diamine yellow, green, red, black, blue, &c.), while Meister, Lucius und Brüning call their substantive colouring-matters *dianil colours*. The Bayer Company have the most numerous and important series of substantive dyes, which they term *benzidine* or *benzo dyestuffs* (*e.g.* benzo azurines, benzo browns, benzo reds, &c.). The Actien-Gesellschaft für Anilin-Fabrikation, Berlin, call these dyes Columbia, Zambesi, &c.

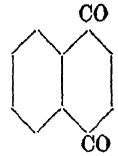
The **Derivatives** (*e.g. sulphonic*) of azoxystilbene, , have the *special property* of dyeing cotton directly in an *acid bath.*

The firm of Meister, Lucius und Brüning, in 1896, placed on the market a class of strongly basic colouring-matters (*Janos dyes*), which colour cotton directly—without previous mordanting—in an *acid bath* and also dye with the same colour the wool and cotton of a mixed fabric when the latter is boiled in a bath acidified with sulphuric acid. These dyes change their tint temporarily if brought into contact with hot objects (hot iron).

Of very great importance is the group of azo-dyes produced directly on the fibre by processes of diazotisation and combination, these bearing the name of **Ingrain Colours.**

Cotton fabrics or yarns are impregnated in the cold with a base (aniline, p-nitraniline, aminoazobenzene, benzidine, safranine, &c.) or they may be first dyed with one of the substantive tetrazo-dyes containing free auxochrome amino-groups (*e.g.* diamine black, primuline yellow, benzo brown, blue, or black, &c.). They are then transferred for 15 minutes to a wooden vessel containing a cold *diazotising* solution, this consisting, per 100 kilos of cotton, of 2000 litres of water, 2 to 4 kilos of sodium nitrite, and 6 to 10 kilos of hydrochloric acid at 20° Bé.; this diazotisation is carried out in dimly lighted rooms, since sunlight readily decomposes the diazo-compounds formed. After removal from this bath, the cotton is allowed to drain for a short time and is then placed in a *developing bath* (*coupling bath*) containing 2000 litres of water, 0·5 kilos of sodium carbonate and 0·5 to 1 kilo of β-naphthol previously dissolved in 415 to 430 grms. of caustic soda at 40° Bé. The cotton is manipulated rapidly and in a few minutes intense development of the colour takes place. When substantive dyestuffs are thus further diazotised on the fibre, they exhibit increased fastness to scouring, and this is still more the case if the fabric is subsequently treated with a bath of potassium or sodium bichromate at 90° to 95° for 20 minutes; a final copper sulphate bath at 50° for 25 minutes gives greater fastness to light; but both copper and chromium compounds diminish the brightness of the colour to some extent, and on this account the firm of Geigy suggests the use of a final bath of formalin. Instead of β-naphthol, α-naphthol, resorcinol, phenylenediamine, *benzonitrole* (diazotised p-nitraniline), &c., may be used. By this method of diazotising and developing on the fibre the original tint of the basic substance is intensified, certain yellows become orange or scarlet (p-nitraniline gives with β-naphthol a fine scarlet similar to Turkey red, while with α-naphthol it yields a violet-red), certain reds become brown or even blue, the blues become intense blacks, &c. Different developers give different colours or shades.

The coupling of a phenol with a diazo-compound is prevented by the presence of a reducer which destroys the latter; as reducing agent stannous chloride was at one time used, but use is now made of sodium or zinc hydrosulphite, which permits of the printing of textiles in white designs on a coloured ground.

III. HYDRAZONE AND PYRAZOLONE COLOURING-MATTERS. Hydrazones are obtained by the action of phenylhydrazine, $C_6H_5\cdot NH\cdot NH_2$, on compounds containing ketonic groups (*see* p. 210). Thus, for example, the condensation of phenylhydrazine with α-naphthaquinone, , gives a hydrazone of the constitution $C_6H_5\cdot NH\cdot N : C_{10}H_6 : O$. The same compound is obtained by the interaction of α-naphthol and diazobenzene, so that its constitution might be that indicated by the equation:

$$C_6H_5\cdot N_2\cdot Cl + C_{10}H_7\cdot OH = HCl + C_6H_5\cdot N : N\cdot C_{10}H_6\cdot OH,$$

one hydrogen atom being mobile and oscillating between nitrogen and oxygen. The hydrazones may hence be regarded as azo-compounds and can be prepared from diazo-derivatives and phenols. This is true for aromatic compounds (which can be diazotised),

but not for those of the aliphatic series, which are only exceptionally diazotised ; in the latter case, the hydrazones must be obtained by means of phenylhydrazine.

The colouring-matters of the hydrazone group have not as yet been practically applied, as they are too weak. It was formerly thought that tartrazin was a hydrazone, but Anschütz showed it to be a pyrazolone. In general the **Tartrazins** are obtained by condensing, in hot acid solution, the aromatic hydrazines (sulphonated) with dihydroxytartaric acid, $CO_2H\cdot C(OH)_2\cdot C(OH)_2\cdot CO_2H$, which probably reacts with phenylhydrazine as a true di-ketone, $CO_2H\cdot CO\cdot CO\cdot CO_2H$, giving

$$\begin{array}{l} CO_2H\cdot C : N\cdot NH\cdot C_6H_4\cdot SO_3H \\ \quad\;\;\vert \\ CO_2H\cdot C : N\cdot NH\cdot C_6H_4\cdot SO_3H \end{array}$$

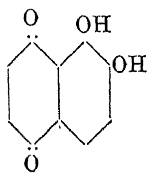
a molecule of water is then lost from a carboxyl- and an imino-group,

$$N \begin{array}{l} \diagup N(C_6H_4\cdot SO_3H)\cdot CO \\ \qquad\qquad\qquad\qquad\quad\;\vert \\ \diagdown C(CO_2H) —— C : N\cdot NH\cdot C_6H_4\cdot SO_3H. \end{array}$$

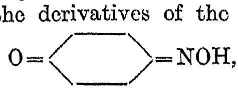
The sodium salt is used as a fast yellow for wool, in an acid bath. Some tartrazin nitrates are fixed also by mordants. In an acid bath tartrazin dyes wool a bright and fairly fast yellow.

IV. COLOURING-MATTERS DERIVED FROM QUINONES AND QUINONOXIMES. All these colouring-matters give very fast tints on fibres mordanted with metallic oxides with which they form lakes. If the hydroxyl groups present are not in the ortho-position with respect to one another and to the chromophore $CO\!<$, the lakes formed have no affinity for the fibres.[1]

The most important colours of this group are formed by introducing into the chromophores, naphthalene groups ; *e.g.* **Naphthazarin**, which is a *dihydroxynaphthaquinone*,



The quinonoximes contain the group $: N\cdot OH$ in place of the ketonic oxygen ; they have properties similar to the hydroxyquinones, and here too the affinity for metallic mordants is most marked in the derivatives of the orthoquinones. A few colouring-matters derived from the oxime



, are known, *e.g. fast green for cotton, naphthol green,* &c.

Among these quinone derivatives are almost all the alizarin (*see* p. 617) and anthracene (*see* p. 615) colouring-matters, purpurin, &c., in all gradations from yellows to reds, blues, blacks, greens, &c.

For hundreds of years **Alizarin** was the sole representative of a group of excellent colours, and was only obtained naturally mixed with purpurin, from which it was separated with difficulty. Nowadays, not only is alizarin prepared artificially, but there are quite fifty other colouring-matters of this group, fast to light and chemical and atmospheric reagents.

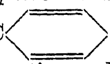
And while nature yields colours such as madder and indigo in an impure condition (as these are secondary products of vegetable life) and not directly applicable for dyeing, the artificial products are highly pure, much brighter in colour and more easily utilisable as dyes.

Alizarin and anthracene dyes, which are the prototypes of *mordant colouring-matters*, are used in large quantities for the fast dyeing of wool for clothing and military uniforms. As a rule the wool is mordanted first, by boiling for an hour with an aqueous solution containing 2 to 3 per cent. of potassium dichromate and 1 per cent. of sulphuric acid and

[1] Mordant colouring-matters are generally obtained with the following groups in the ortho-position : OH and NO (or CO and NOH), 2NOH, 2OH. Also, according to Noelting (1909), in the anthraquinone series intense mordant dyes are obtained also with OH and NH_2 in the ortho-position (less important and less intense are those with OH and NH_2 in the para-position).

amounting to 15 to 20 times the weight of the wool. After mordanting, the wool is rinsed well in water and dyed in a solution of the dyestuff faintly acidified with acetic acid ; this bath is heated very gradually to boiling, the latter being maintained for 1 to 2 hours to obtain the maximum intensity and fastness. If fresh addition of the colouring-matter is necessary in order to obtain the desired shade, it is best first to lower the temperature of the bath to 40° to 50° with cold water in order to prevent non-uniformity of tint.

V. DIPHENYL- AND TRIPHENYL-METHANE COLOURING-MATTERS,

$CH_2{<}{}^{C_6H_5}_{C_6H_5}$ and $C_6H_5{-}CH{<}{}^{C_6H_5}_{C_6H_5}$. It has been shown on p. 647 that in these colouring-matters the *chromophore* consists of the benzene group with two double linkings in the para-position, R=C=.

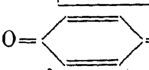
The mode of formation and the general properties of diphenyl- and triphenyl-methane derivatives were described on pp. 606, 607.

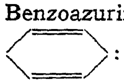
In this group are found **Auramine** (basic) and **Pyronine** (also basic) which dye wool in an acid bath and cotton mordanted with tannin.

The rosaniline group embraces all the basic colouring-matters derived from triphenylmethane, *e.g. malachite green, methyl violet, formyl violet, fuchsine,* &c., while with sulphonic and other groups, acid dyes are obtained, such as *patent blue (carmine blue), acid fuchsine,* &c.

There are also azo-derivatives of triphenylmethane, such as **Rosamine**, which dyes silk violet-red with a yellow fluorescence, and has the formula :

$$C_6H_5\cdot C{<}{}^{C_6H_3[N(CH_3)_2]}_{C_6H_3[N(CH_3)_2Cl]}{>}O.$$

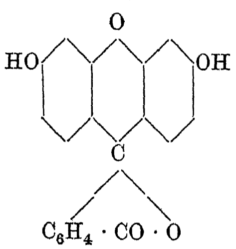
The **Rosolic Acid** group, O=$=C{<}{}^{C_6H_3(CH_3)\cdot OH}_{C_6H_4\ OH}$, formed by fusion of phenol with oxalic acid in presence of concentrated H_2SO_4, also furnishes numerous colouring-matters, *e.g. aurine, coralline, pittacal, chrome violet.*

Benzoazurin is formed from 1 mol. of phenylchloroform with 2 mols. of phenol : O :  $: C{<}{}^{C_6H_4\cdot OH}_{C_6H_5}$; these colouring-matters have no practical application and are obtained by the condensation of phenols with phthalic anhydride :

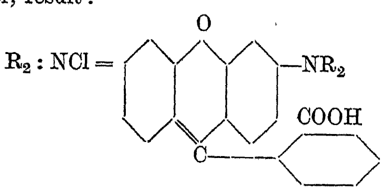
$$C_6H_4{<}{}^{CO}_{CO}{>}O + 2C_6H_5\cdot OH = H_2O + C_6H_4{<}{}^{C(C_6H_4\cdot OH)_2}_{CO}{>}O.$$

Phenolphthalein

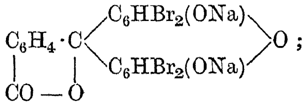
Phthaleins (*see* p. 581) with the hydroxyls in the para-positions are of some importance ; if resorcinol, $C_6H_4(OH)_2$, is used in place of phenol, **Fluorescein** is obtained :



while if dimethylaminophenol is taken instead of resorcinol, or if fluorescein chloride is heated with a secondary amine, NHR_2, fine red colouring-matters, **Rhodamines**, which are basic in character, result :

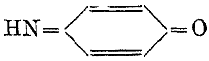


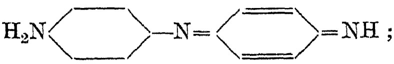
If previously brominated phthalic anhydride is used, the **Eosins** are obtained :

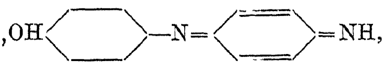
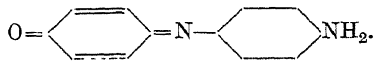


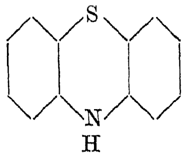
these give beautiful fluorescent red colours on silk but are not very fast to light (*see* p. 581).

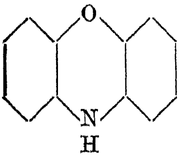
VI. COLOURING-MATTERS OF THE QUINONIMIDE GROUP. To this belong the derivatives of indophenol and indamine.

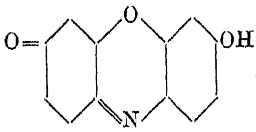
Of the hypothetical quinonimides,  and , various derivatives and condensation products are known, *e.g.* **Indamine,**

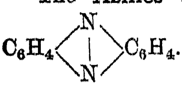


Indophenol,  

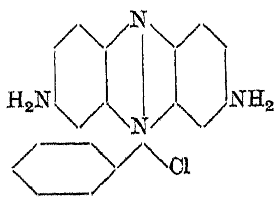
The **Thiazones,** *e.g. thiodiphenylamine,* , with indamines form **Thiazimes** (*e.g. Lauth's violet* or *thionine, methylene blue, methylene green,* &c., which are basic dyes).

The **Oxamines** and **Osazones** have an oxygen atom in place of the sulphur of thiazones, , and undergo various condensations : *Capri blue, naphthol blue, Nile blue,* &c., which are also basic.

The **Cyanamines** are related to Nile blue ; **Resorufin** is an osazone, namely, hydroxy-diphenosazone,  ; **Gallocyanine,** $C_{15}H_{12}O_5N_2$, is obtained by heating nitrosodimethylaniline with gallic acid in alcoholic solution. They dye chrome-mordanted wool a very fast violet, and are used in printing linen, which is treated with sodium bisulphite and chromium acetate and subsequently steamed.

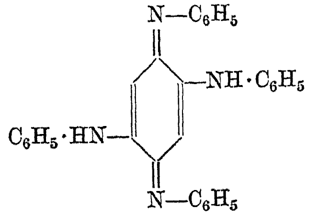
The **Azines** were formerly called **Safranines** ; the simplest type is **Phenazine,** . The *eurodines* are used for dyeing cotton mordanted with tannin.

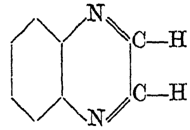
The **Safranines** contain four nitrogen atoms and three aromatic nuclei :

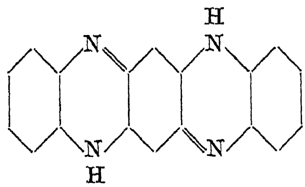


and are strongly basic and give red colours on cotton mordanted with tannin.

Indulins are obtained by heating aniline hydrochloride with aminoazobenzene. The following constitution has recently been established for one of the indulins :



The **Quinoxalines** contain the nucleus  ; the **Fluorindines** can be represented by the formula:



VII. ANILINE BLACK. The oxidation in various ways of aniline salts in acid solution gives aniline black, which is of considerable importance in the dyeing of cotton.

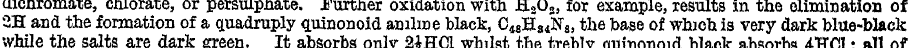
Among the different oxidising agents, a special place is occupied by vanadium salts (suggested by Witz in 1877), which bring about the oxidation of large quantities of aniline (transferring oxygen by catalytic action) ; 1 part of vanadium, in presence of a sufficiency of potassium chlorate, oxidises as much as 270,000 parts of aniline hydrochloride. In point of efficiency, vanadium is followed by caesium and then copper, the action of iron being much less.

Aniline black has a feebly acid character and is insoluble in almost all solvents. It dissolves with difficulty in aniline and forms with it a violet and then a brown colour ; phenol dissolves it more easily, giving a green coloration. With fuming H_2SO_4, it yields soluble, coloured sulpho-compounds. Acetic anhydride gives a faintly coloured acetyl-derivative, and potassium dichromate a violet-black product. When treated with permanganate and then with oxalic acid, aniline black is partially decolorised. Energetic reducing agents (Sn + HCl) decompose it completely.[1]

[1] The *chemical constitution of aniline black* has been the subject of much discussion. Assuming that the first intermediate product of the oxidation of aniline is aniline black (Nietzki), it cannot be true, as is often thought, that the transformation of aniline into quinone by oxidation takes place through the intermediate stages of phenylhydroxylamine and p-aminophenol, since these do not yield aniline black on oxidation, phenylhydroxylamine giving a nitrosobenzene and not a quinone; nor can aminodiphenylamine (Nover, 1907) be formed, since this, on oxidation, gives emeraldine, a compound never obtained in the oxidation of aniline. It has now been found possible to convert aniline black to the extent of 95 per cent. into quinone by oxidising with lead peroxide (chromic acid giving less than 80 per cent.), so that the indaminic formula (proposed by Bucherer, 1907) can no longer be attributed to aniline black, since, according to this, it would give only 50 per cent. of quinone. This result led R. Willstätter and S. Dorogi (1909) to suggest for aniline black the formula $(C_6H_4N : C_6H_4 \cdot NH)_4$, *i.e.* $C_{48}H_{36}N_8$, which is confirmed by the fact that the oxidation requires $1\frac{1}{4}$ atom of oxygen per molecule of aniline with a yield of 97 per cent. Further, the determination of the molecular weight by hydrolysis of aniline black with dilute sulphuric acid at 200° indicates clearly the separation of one-eighth of the nitrogen as ammonia :

$$C_6H_4N : C_6H_4 : NH + H_2O = C_6H_4N : C_6H_4 : O + NH_3.$$

All these results point to the trebly quinonoid formula of aniline black as the most probable :



This aniline black is obtained by oxidising aniline in the cold with rather less than the theoretical quantity of dichromate, chlorate, or persulphate. Further oxidation with H_2O_2, for example, results in the elimination of 2H and the formation of a quadruply quinonoid aniline black, $C_{48}H_{34}N_8$, the base of which is very dark blue-black while the salts are dark green. It absorbs only $2\frac{1}{2}$HCl whilst the trebly quinonoid black absorbs 4HCl; all of the latter are displaced by ammonia, which, however, in the former case, leaves 1HCl (4·5 per cent. of Cl in the nucleus). In practice the quadruply quinonoid black is obtained with excess of a slow oxidising agent acting in the cold, *e.g.* with chlorate and copper sulphate or with chlorate and vanadium. On hydrolysis, the quadruply quinonoid black also loses one-eighth of its nitrogen as ammonia, forming the more complete black, $C_{48}H_{33}ON_7$, which is not turned green by SO_2. Oxidation of the corresponding product of hydrolysis of the trebly quinonoid black gives the same quadruply quinonoid black, $C_{48}H_{33}ON_7$. The practical preparation of aniline black in a single bath leads to the quadruply quinonoid black that turns green, and further oxidation of this in the hot yields the black

In practice aniline black is produced directly on the fibre and the use of this very stable colouring-matter is due especially to the studies and initiative of Prud'homme, C. Koecklin, Paraf, &c.

After many improvements, the production of aniline black (termed also *oxidation black* or *fine black*) directly on cotton fibre is now carried out as follows (the quantities given are for 50 kilos of cotton). The three following solutions are prepared separately: I. 5·5 kilos of aniline oil (*see* p. 558) + 6·25 kilos of commercial HCl + 50 litres of water; II. 3·5 kilos of sodium (or potassium) chlorate + 50 litres of water (1·5 kilo of starch is sometimes added); III. 3 kilos of potassium ferrocyanide in 20 litres of water. When cool, the solutions are mixed (1 grm. of vanadium chloride is sometimes introduced) and the yarn or fabric immersed until it is well soaked. It is then gently pressed and passed slowly over rollers through the oxidation chamber (*see illustration given later*) so that at least an hour elapses before it emerges at the opposite end. The temperature of the chamber should not exceed 50° and the humidity 25°. The fabric assumes a coarse greenish colour, which is changed to a fine black when it is transferred to a *Jigger* (*see later*) containing 2 kilos of potassium dichromate, 250 grms. of sulphuric acid and 100 to 120 litres of water at the temperature 50°. The black thus obtained, when thoroughly washed, is turned green only to a slight extent in the light.

VIII. QUINOLINE AND ACRIDINE COLOURING-MATTERS. [Among the quinoline dyestuffs are *quinoline yellow* (water- or alcohol-soluble), *quinoline red*, *cyanine*, &c.; all of them contain one or more of the chromophores, $C_6H_4\left<\begin{matrix}CH : CH\cdot \\ N : CH\end{matrix}\right.$, or its homologues.

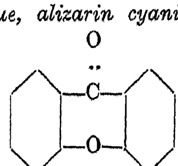
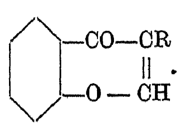
Acridine derivatives possibly contain a quinonoid chromophore of the formula $RC\left<\begin{matrix}C_6H_3(: NH) \\ C_6H_4\end{matrix}\right>NH$.

They are obtained by condensing m-diamines with formaldehyde, heating the resulting tetraminodiphenylmethane with acid to remove ammonia, and finally oxidising with ferric chloride.] To this group belong *acridine orange* and *yellow*, *phosphine*, *benzoflavin*, &c.

IX. THIAZOLE COLOURS. These contain the group $\begin{matrix}=C-N \\ | \\ =C-S\end{matrix}\!\!>C-$ with the chromophore $-C{=}N-$ and are formed by heating p-toluidine with sulphur, the resulting **Primulin** being probably of the constitution

$$CH_3\cdot C_6H_3\left<\begin{matrix}N \\ S\end{matrix}\right>C\cdot C_6H_3\left<\begin{matrix}N \\ S\end{matrix}\right>C\cdot C_6H_4\cdot NH_2:$$

it may be easily sulphonated, dyes cotton directly and may be diazotised and developed on the fibre (*see* p. 658). The methyl derivative is **Thioflavin**. These colouring-matters are not very fast against light.

X. COLOURING-MATTERS OF THE OXYKETONES, XANTHONE, FLAVONE, COUMARIN. This group embraces many valuable mordant colouring-matters: *alizarin yellow*, *anthracene yellow*, *alizarin black* (*see* Alizarin Colouring-Matters, p. 659), *flavopurpurin*, *alizarin green*, *alizarin blue*, *alizarin cyanine*, *anthracene blue*, &c. The characteristic group of the xanthones is , and that of the flavones .

Indian yellow is a hydroxy-derivative of xanthone.

XI. INDIGO, INDIGOIDS, AND OTHER NATURAL COLOURING-MATTERS. In addition to what has been stated with reference to indigo (*see* p. 639 *et seq.*), it may be said that there are a number of derivatives of artificial indigo which are reduced with hydro-

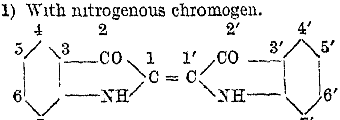
which does not turn green, the terminal imino-group being hydrolysed. This latter black is obtained also by the two- (or more) bath process or by steaming. Oxidation of aminodiphenylamine instead of aniline gives first the reddish blue imine (C_{24} . . . .), *emeraldine*, which then polymerises, forming the black (trebly quinonoid).

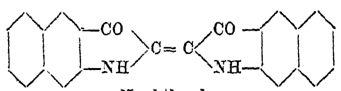
sulphite and alkali and give very fast colours which are superior to indigo and resist even concentrated solutions of chloride of lime.[1]

The **Indanthrene Colours**, which were at first very expensive, are now obtainable at more reasonable prices and give medium and dark shades. They are so resistant to various reagents that they are used as pigments in place of ultramarine, &c. ; they are used also for blueing sugar and other foodstuffs, as they are fast to light and non-poisonous.

[1] Bohn has given the name *vat dyestuffs* to those insoluble pigments the molecule of which contains at least one ketonic group capable of being reduced (*e g* by hydrosulphites), taking up hydrogen and thus becoming soluble in an alkaline liquid and fixable by animal and vegetable fibres. These vat dyestuffs may be divided into two classes : *indigoids* and *indanthrene derivatives*. The first class comprises two series : *symmetrical* (indigo, &c.) and *unsymmetrical* (indirubin, &c), and each series contains various families of the following types, to all of which the chromogen, —CO—C=C—CO, is common.

(1) With nitrogenous chromogen.

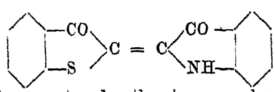




Naphthindigo

Indigo and its halogenated and other substitution derivatives : chloro-, bromo-, alkyl-, and naphthol-indigo. The substitution takes place in the benzene nucleus ; many polybromo-derivatives are formed. The colours range from reddish blue to greenish blue. The *antique purple* recently studied by Friedlander is 6 6′-dibromoindigo. 5-Bromoindigo (*pure indigo R*), 5 5′-dibromoindigo (*pure indigo 2B*), 5 : 7 : 5′-tribromoindigo (*Ciba blue B*), 5 : 7 . 5′ : 7′-tetrabromoindigo (*Ciba blue 2B* or *indigo 4B*) have been prepared.

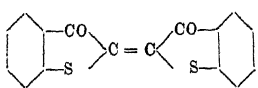
(2)



Mixed symmetrical with nitrogen and sulphur chromogens

Besides the chromophore $\genfrac{}{}{0pt}{}{CO}{NH}\!>\!C=$ of indigo, these have also the chromophore $=C\!<\!\genfrac{}{}{0pt}{}{CO}{S}$. Belonging to this family are : *Ciba grey G* (monobromo-derivatives), *Ciba violet R, B, 3 R* (these are polybromo-derivatives of *Ciba violet A*).

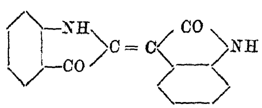
(3)



Symmetrical with sulphur chromogen

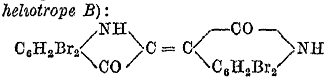
The first term is Friedlander's *thioindigo* (or *thioindigo red B*) ; *Ciba bordeaux B* (5 : 5′-dibromothioindigo) and numerous derivatives in which the 5- and 5′-positions are occupied by alkoxy- and thioalkyl-groups have been prepared, among these being red and brown colours and the various colours of the helindone series of Meister Lucius und Bruning.

(4)

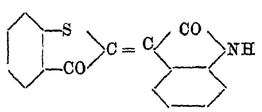


Indirubin with asymmetric nitrogen chromogen

Indirubin is not a colouring-matter, since on reduction it forms indigo. But use is made of *tetrabromoindirubin* (*Ciba heliotrope B*):

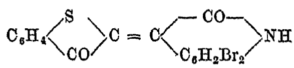


(5)

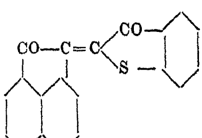


Thioindigo scarlet R

The dibromo-derivative forms *thioindigo scarlet G* (or *Ciba red G*) :

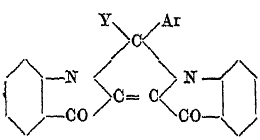


(6)



Is known by the name of *thioindigo scarlet* 2 *G* (*Ciba scarlet G*).

(7)

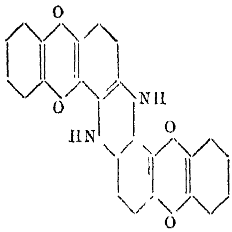


This is a new family which has given the first yellow colours of the indigoid group (*Ciba indigo yellow* 3 *G* and *Ciba yellow G*, which is a dibromo-derivative of the preceding). The group Ar is the benzoyl residue, but it is not known whether Y is H or OH, or whether it represents a double linking to the nitrogen atom.

Materials dyed with indanthrene dyestuffs do not stand heating in an autoclave with alkali, the colours being reduced and rendered soluble. The Badische Anilin- und Soda-

The second class is that of the anthracene derivatives, with the following families:

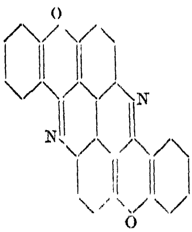
(1)



Indanthrene blue

Indanthrene is formed by condensing 2 mols. of aminoanthraquinone by means of fused alkali and is a *dianthraquinonedihydroazine*. With reducing agents, partial reduction of the ketonic group occurs, dihydroindanthrene becoming soluble in alkali and dyeing cotton directly. The halogenated derivatives are of a more greenish blue, resistant to oxidising agents and to chlorine. Use is made of *indanthrene blue GC, GCD*, 3 *G*, and 3 *RC* and of *algol blue* and *algol green*. The GCD blue is obtained by boiling indanthrene with aqua regia. *Anthraflavone* (yellow) is similar to indanthrene, but without the NH groups.

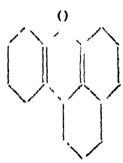
(2)



Flavanthrene

Flavanthrene (or *indanthrene yellow G* and *R*) is obtained by oxidising 2-aminoanthraquinone with antimony pentachloride in boiling nitrobenzene solution. An analogous compound which has an orange-yellow colour and in which the two nitrogen atoms are replaced by CH, is *pyranthrene* (or *indanthrene golden orange G*), the halogen derivatives of which tend to red; of these, *dibromopyranthrene* (or *indanthrene scarlet G*) is used.

(3)



Benzanthrone

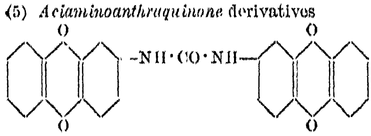
Benzanthrone is obtained by condensing anthraquinone or its derivatives with glycerol in presence of concentrated H_2SO_4. Benzanthrone and its halogen derivatives are not colouring-matters, but by various condensations they lead to excellent colouring-matters, such as *violanthrene*, the dibromo-derivative of which is *indanthrene green B*; *isoviolanthrene* (which has a similar constitution to pyranthrene) and its dichloro-derivative (*indanthrene violet RR extra*).

(4)

Anthraquinonimide derivatives

Indanthrene bordeaux and *indanthrene red G* and *R* are formed from 3 mols. of anthraquinone joined in various ways by two imino-groups. *Algol red*, which was the first red vat dyestuff of the anthraquinone series, consists of 2 mols. of anthraquinone united by an NH group, one of them being condensed with a pyridone ring.

(5) *Acicaminoanthraquinone* derivatives



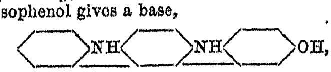
Helindone yellow 3GN

Characteristic of these is the complex of several NH groups united once or more times to CO groups. *Helindone yellow* 3 *G* represents two anthraquinone groups condensed with urea. Various other condensations of aminoanthraquinones with benzoyl, succinic, tartaric, phthalic, &c., groups give *algol reds G, R*, and 5 *G*, &c.

(6)

Various types: ***Rufanthrene, leucol, cibanones, hydrones, indigolignoids***

These colouring-matters are obtained by fusing aminoanthraquinones with sulphur or alkaline sulphides (*rufanthrene* browns, greys, olives), *indanthrene brown, cibanone brown, cibanone yellow*; the first *cibanone black* was obtained from methylbenzanthrene, and the *leucol* colours of the firm of Bayer are also of this group. A mixed indigoid-anthracene group has recently been obtained. Thus, the action of isatin chloride, &c., on α-naphthol (or its ortho-derivatives) gives the indigoid colouring-matter and an isomeride of analogous properties, *e.g. indonaphthalene* or *indolignone* (Friedländer and Bezdzich, 1909); both the indigoid and the indolignone are decomposed by alkali into anthranilic acid and the corresponding hydroxynaphthaldehyde. A group of sulphur vat dyestuffs is that of the *indrone blues* (Cassella), derived from carbazole, which with p-nitrosophenol gives a base,



and this, when fused with sulphur or sulphides forms reducible colouring-matters soluble in alkali.

Fabrik recommend the addition of an oxidising agent to the autoclave bath to prevent the reduction.

The principal natural *mordant* colouring-matters are: logwood, brazilein, archil, cochineal, catechu, sandalwood, &c.; and the natural *substantive* dyes for cotton and wool are: bixin, curcumin, carthamin, &c.

These dyewoods are placed on the market in small trunks or in chips; for economy in transport and convenience in use, dense aqueous or concentrated dry extracts are often prepared. Italy imported the following quantities:

	1906	1907	1908	1909	1910	
	quintals	quintals	quintals	quintals	quintals	
Woods for dyeing and tanning	223,762	273,272	219,985	275,300	266,400	(£140,000)
Dye extracts	7,883	7,540	5,573	6,699	6,412	(£23,080)
Catechu and gambier	5,603	4,025	3,998	4,587	5,806	(£13,935)

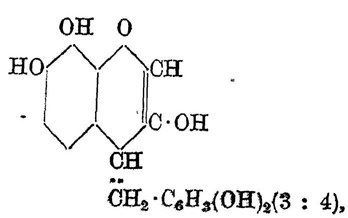
Germany's imports and exports were as follow:

	Imports		Exports	
	1908	1909	1908	1909
	quintals	quintals	quintals	quintals
Logwood	111,165	94,489	14,046	8,563
Yellow wood	7,697	9,424	1,372	1,016
Red-wood	7,245	11,266	2,030	812
Catechu	33,852	35,438	2,426	2,425

LOGWOOD or Campeachy is obtained from the barked trunk of a tree (*Hæmatoxylon campechianum*; Fig. 423 shows twig, leaves, flowers, and seeds) which grows in Central America and in the Antilles, the best qualities being those of Honduras, San Domingo, and Jamaica. Just as the consumption of indigo has not diminished in spite of the competition of the numerous artificial aniline and alizarin colours, so also the use of logwood in dyeing tends to increase, although not in similar proportion to that of the artificial dyes. The wood arrives in Europe in logs weighing 150 to 200 kilos, which are sawn into short pieces, chopped and reduced to chips or raspings; more rarely they are ground.

The colouring-matter of logwood was studied by Chevreul in 1810, by Erdmann in 1842, and by Hess and Reim in 1871. It consists of a glucoside which occurs in the *fresh* wood and which, perhaps by simple fermentation or by the action of water and air, separates the base of the colouring-matter, *i.e.* Hæmatoxylin, $C_{16}H_9O(OH)_5$, and this, under the influence of atmospheric oxygen (best in presence of alkali), gives the colouring-matter *hæmatein* (which dyes with metallic oxides), $C_{16}H_{12}O_6$, 2H being thus lost. Hæmatein is moderately soluble in water, alcohol, ether, or glacial acetic acid, and insoluble in chloroform or benzene. In ammoniacal solution it assumes a purple-red colour, which becomes brown in the air. By reducing agents (H_2S, SO_2, Zn + HCl, &c.) hæmatein is decolorised without, however, giving hæmatoxylin.

Hæmatoxylin is probably 3 : 4 : 3′ : 4′-Tetrahydroxyrufenol:



and hæmatein would have a quinonoid formation in place of the hydroxyl of the first nucleus, H being lost together with another H from the para-CH of the second nucleus.

In dyeing, logwood is used in chips or as an extract. The chips are first matured (? fermented) by moistening with water, heaping up and stirring every two or three days for one or two weeks, care being taken to prevent heating of the mass, which would destroy the colouring-matter. The wood changes from a yellowish to a brownish red colour and is extracted with boiling water, to which it gives up 2·5 to 3 per cent. of its weight; the solution, which is rich in hæmatein, is used as it is in the dye-vat. Logwood extracts are prepared by boiling the non-fermented wood with water in open boilers or in autoclaves and concentrating the solution *in vacuo* to 30° Bé.; these extracts are very rich in hæmatoxylin.

Hæmatein is a mordant colouring-matter, *i.e.* is fixed and gives intense and fast colours only on mordanted fibres, and is generally used for black or blue-black shades with various shot effects, according to the nature of the mordant: with aluminium salts it gives a greyish violet-black, with chromium salts blue-black, with iron salts grey-black, with copper salts greenish blue-black, and with tin salts violet-black.

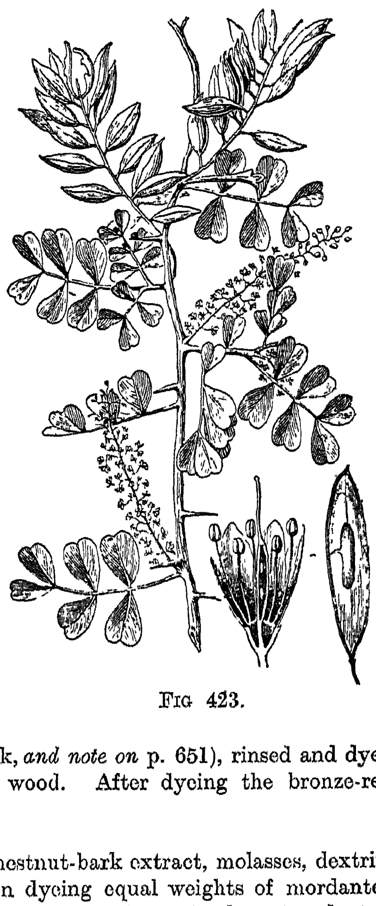


FIG 423.

A fine black is usually obtained by mordanting, *e.g.* wool, for 2 hours in a boiling bath containing 2 to 3 per cent. of potassium dichromate, 3 to 4 per cent. of tartar (or 2 per cent. sulphuric acid, 3 per cent. lactic acid, &c.) and 0·5 to 1 per cent. of copper sulphate (all calculated on the weight of fabric). The mordanted fabric is well washed and dyed in a boiling aqueous bath, to which is added the dilute logwood extract or 5 to 8 per cent. of the concentrated extract or the matured chips in bags. To obtain black-black (coal-black without blue reflection), 0·2 to 0·5 to 1 per cent. of Cuba yellow wood extract is added. Dyeing is followed by thorough washing in cold water.

Cotton is first mordanted in the usual way in a tannin bath (2° to 3° Bé. overnight), then passed into an iron nitrate bath (*see* Dyeing of Silk, *and note on* p. 651), rinsed and dyed in the hot aqueous bath with logwood and yellow wood. After dyeing the bronze-red appearance is removed by a soap bath.

For dyeing silk black, *see later*.

Logwood extracts are often adulterated with chestnut-bark extract, molasses, dextrin, sumac, &c., and as a rule the best test consists in dyeing equal weights of mordanted fabric with equal weights of the suspected and a pure extract. Sugar (molasses) or dextrin may be detected by precipitating with a slight excess of lead acetate and examining the filtrate by means of either Fehling's solution or the polarimeter.

Chestnut-bark extract is detected by treating 1 grm. of the extract, dried at 100°, with ether and weighing the portion dissolved by the ether. The residue is then extracted with absolute alcohol and the amount dissolved determined. A good, dried extract contains 86 to 88 per cent. of matter soluble in ether and 12 to 14 per cent. soluble in alcohol, while, if chestnut-bark extract is present, less dissolves in ether and more in alcohol.

Statistics. *See above.*

ARCHIL is extracted from *Roccella tinctoria* (2 to 12 per cent.) or from other lichens growing on the coast or on bare rocks in mountainous districts. The red colouring-matter is formed after fermentation in presence of a little ammonia, and after the action of atmospheric oxygen. Prior to fermentation, the colourless compounds contain roccellic acid (p. 305) and erythric acid, while, after the decomposition, orcin (*see* p. 544) is present; the latter,

when oxidised in presence of NH_3, gives orceine (*see* p. 544), which forms violet-red lakes. Archil is placed on the market as extract or solid preparation.

Cudbear (or *perseo*) is obtained from *Lecanora tartarea* and dyes wool and silk very uniformly in presence of alum, tin salt, and tartaric acid.

Litmus (or *tournesol*) is formed from orcin by the action of ammonia or soda, and is obtained from various lichens (*Roccella tinctoria*). The extract is mixed with gypsum or chalk and made into tablets, which contain also various colouring-matters (*azolitmin, erythrolein, erythrolitmin, spaniolitmin*). It is very sensitive to acids, which redden it, and to alkalis, which turn it blue, and hence serves as an excellent indicator.

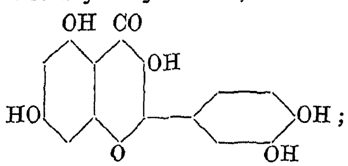
COCHINEAL has been long used as a colouring-matter and is the female of the insect *Coccus cacti*, which lives on the cactus of the Canary Islands, Algeria, Java, Guatemala, &c. When the insect is three months old (weight = 0·0065 grms.) it is killed with hot water, (*black grain*) or in an oven (*silver grain*). The colouring-matter is **Carminic Acid**, $C_{17}H_{16}O_{10}$. The dry insects are powdered and extracted several times with boiling water, the dye-bath being prepared with hot water, 3 per cent. of oxalic acid and 1·5 per cent. of tin salt; the wool is immersed in this for at least 30 minutes at a boiling temperature. The wool may be first mordanted separately with oxalic acid and tin salt and then dyed in the aqueous cochineal. Italy imported 47 quintals of cochineal and kermes in 1906; 24 in 1908, and 33 (£330) in 1910.

YELLOW WOOD or **Cuba Wood** (*Old fustic*) is obtained from the trunks of *Morus tinctoria* or of *Maclura tinctoria* of the West Indies, Brazil, and Mexico, the best kinds being, however, those of Cuba, Tampico, Porto Rico, and Jamaica. The colour may be extracted from the wood by means of steam, and the concentrated extract contains a tanning material (*maclurin*), since a brighter yellow is obtained on dyeing if a little gelatine is added to precipitate this tanning substance; if this is not done, prolonged boiling gives dark or brownish shades. Although *Cuba yellow* dyes pure fibres directly, really fast colours are obtained only by chrome mordanting, &c.; hence Cuba yellow is used together with logwood or even alizarin or anthracene colouring-matters.

Statistics. *See above.*

QUERCITRON is sold in small chips or, better, as a coarse powder obtained by grinding the bark—freed from epidermis—of *Quercus tinctoria* and *Q. nigra*, which grow in Pennsylvania, Carolina, Scotland, France, and the South of Germany.

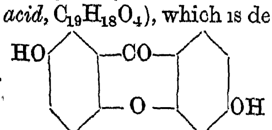
The dilute aqueous extract does not keep, and must hence be used immediately. Chevreul separated from the bark the compound **Quercitrin**, $C_{21}H_{22}O_{11} + 2H_2O$, which when boiled with acid takes up 1 mol. H_2O, giving **Quercetin**, $C_{15}H_{10}O_7$, and **Isodulcitol**, $C_6H_{14}O_6$. Quercetin is 1 : 3 : 3′ : 4′-**Tetrahydroxyflavanol**,



it dissolves in alkali, giving an orange-yellow coloration and yields phloroglucinol and protocatechuic acid when fused with alkali. It is sulphonated by concentrated sulphuric acid, forming a direct dye for wool.

It dyes more especially animal fibres (wool) either previously mordanted or with an alum or chrome mordant added to the dye-bath. Similar behaviour is shown by *flavin*, which is a more concentrated preparation of quercitron and contains quercetrin and quercetin.

Natural **INDIAN YELLOW** is still extracted in Bengal from the evaporated residue of the urine of cows fed on mango leaves. It contains a hydroxyl derivative of *xanthone*, namely, **Euxanthone**, as glycoronic ester (*euxanthinic acid*, $C_{19}H_{18}O_4$), which is decomposed by hot hydrochloric acid into **Euxanthine**, $C_{13}H_8O_4$ or



(obtained synthetically by condensing hydroquinonecarboxylic acid with β-resorcylic acid).

Natural Indian yellow functions as a mordant dyestuff, but is now scarcely used for textiles as it is not very stable to light.

BRAZIL WOOD or **Red Wood** is obtained from the trunk of *Cæsalpina brasiliensis* and other varieties. The colourless glucoside it contains gives, on fermentation or when treated with acids, glucose and **Brazilin**, $C_{16}H_{14}O_5$ or $C_6H_3(OH)_2 \cdot C_4H_4O \cdot C_6H_5O_2$, which is coloured carmine by alkali and decolorised by acids or reducing agents, it gives intensely coloured lakes and oxidises in the air, forming **Brazilein**, $C_{16}H_{12}O_5$, while with concentrated nitric acid it gives trinitroresorcinol and, when fused with alkali, resorcinol. It is a red mordant (alum or chrome) colouring-matter, but is only slightly fast to light.

Brazilin seems to have a constitution analogous to that of hæmatoxylin (*see* p. 666) with a hydroxyl group less in the first benzene nucleus, brazilein being apparently the corresponding quinonoid derivative similar to hæmatein (*see above*).

SANDALWOOD is the wood of *Pterocarpus santalinus*, which grows in Madagascar, tropical Asia, and Ceylon. **Santalin** or **Santalic Acid**, $C_{17}H_{16}O_6$, which forms the colouring-matter of this wood, occurs in abundance in other plants (in barwood or *Baphia nitida* of Sierra Leone and in *camwood* or *kambewood* from West Africa).

Santalin gives resorcinol, acetic acid, &c., when fused with alkali, but its constitution is not yet established. It is a mordant colouring-matter, like logwood, and was once used with alizarin to dye cotton red.

CATECHU (or **Cutch**) and **GAMBIER** are extracted from various plants of India, Bengal, Malay, &c. (palm, mimosa, Rubiaceæ, *Acacia catechu*, *Areca catechu*, *Uncaria gambier*, &c.). They contain tannin and colourless catechol, partly combined to a brown colouring-matter. When fused with alkali, they give phloroglucinol, pyrocatechol, and protocatechuic acid. With various mordants they give stable browns or olives, which do not, however, withstand chlorine or alkali. On cotton they give reddish or yellowish brown colours which become fast to light after treatment with alkali dichromate at 60° to 70° (*khaki* used for uniforms in the British, German, and Italian armies).

Nowadays a much faster khaki is obtained by impregnating the white fabric in a cold concentrated bath of pyrolignite of iron, chromium acetate, and a very small proportion of manganese chloride, drying it thoroughly, immersing it in a boiling bath of caustic soda (11° Bé.) and a little sulphoricinate, and oxidising in a hot-air chamber or by means of dichromate solution. With a less concentrated soda bath or one not boiling, the metallic oxides would be precipitated superficially on the fibre, and the dry fabric would be dusty and would wear out sewing needles.

This khaki is very fast against light, scouring, and chlorine, but does not *resist perspiration* (test with a mixture at 1° Bé. of hydrochloric, formic, and acetic acids for 5 hours). *Fastness to perspiration* is given by boiling the dyed fabric for 2 hours in a silicate bath at 6° to 7° Bé.

Statistics. *See above.*

CHLOROPHYLL is not a colouring-matter for textiles but is the green pigment which occurs in many plants (those which assimilate CO_2) and brings about the transformation of the carbon dioxide into starch in the leaves under the action of sunlight—especially of certain rays of the spectrum—and apparently also with the help of an enzyme (Willstätter and Stoll, 1911) known as **Chlorophyllase.** With starch, wax, &c., it forms the characteristic chlorophyll granules of green leaves.

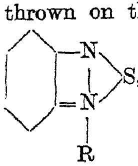
It is soluble in oil, alcohol, ether, or chloroform, its solutions showing blood-red fluorescence and readily undergoing change. Its constitution is still uncertain, and it does not appear to contain combined iron as was formerly thought. Following the indications of the botanists Borodin (1882) and Monteverde (1893), Willstätter and Benz (1908) obtained a pure chlorophyll[1] (2 grms. from 1 kilo of dried leaves) in dark, bluish black crystals with a metallic lustre, which are insoluble in petroleum ether but soluble in alcohol or ether, giving a bluish fluorescence. The green solution of this product, which exhibits the same spectrum as the chlorophyll of fresh leaves, is turned brown by alkali, but again becomes green. Its formula is probably $C_{55}H_{72}O_6N_4Mg$, and the magnesium present (3 per cent.) is perhaps the cause of the catalytic action effecting the transformation of CO_2 into starch; it does not contain phosphorus, as many, including

[1] As chlorophyll readily undergoes change, it is extracted in the cold with methyl alcohol from the carefully dried, powdered leaves (Willstätter), previously washed with petroleum ether. In order to separate it from other colouring impurities, its alcoholic extract is suitably diluted and extracted with ether (benzene or carbon disulphide), many of the impurities remaining dissolved in the alcohol; or the alcoholic extract may be shaken with a large amount of water, which dissolves the chlorophyll in the colloidal state, the decanted aqueous solution being treated with salt and extracted with petroleum ether containing a little alcohol. From this solution the chlorophyll is deposited pure if the whole of the alcohol is eliminated by washing.

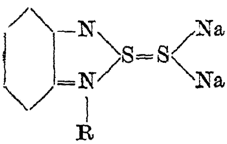
Stoklasa, have thought. Acids remove all the magnesium, the residue being **Phœophytin**, which is similar to chlorophyll, is ethereal in character, and forms various products (*e.g.* *phytol*, *phytochlorin*, and *phytorodin*) when hydrolysed with alkali. **Phytol** forms one-third by weight of the chlorophyll of plants and is a primary, unsaturated, monohydric alcohol, $C_{20}H_{40}O$. Plants produce also an amorphous chlorophyll which, unlike the other, gives phytol on hydrolysis. It is thought that it is analogous in chemical composition to the colouring-matter of the blood (*see later*), since both yield pyrrole when distilled with zinc dust. Willstätter and Isler (1911) showed that chlorophyll contains two colouring-matters: (*a*) bluish green and (*b*) yellowish green, thus confirming the hypotheses of Stokes (1867 and 1873) and of Tswett (1906); the two colours are separated by more or less dilute alcohol. Chlorophyll is used in practice to colour oils, soaps, fats, preserved vegetables, &c.; it costs 8*s*. per kilo or, for the highly purified product, 80*s*. per kilo.

XII. SULPHUR COLOURING-MATTERS. These colouring-matters, which have been discovered since 1893, are very fast on cotton, which they dye directly without a mordant, but in alkaline and reducing solution (sodium sulphide and sometimes a little glucose) which prevents any unevenness which might be produced in the colouring owing to contact with the air. The sulphur colouring-matters do not dye wool or silk in presence of sodium silicate (or of blood or diastofor), so that two colours can be obtained on wool and cotton fabrics, the wool being dyed first with an acid dyestuff and the cotton subsequently with a sulphur colouring-matter in a bath of sodium sulphide and silicate (or blood or diastofor).

They are obtained by melting together sulphur or sodium sulphide and various other colouring-matters or other organic compounds. *Cachou de Laval* has been known since 1873 but has been used but little It was obtained by Croissant and Bretonnière by fusing sawdust, bran, or the like with sodium sulphide. In 1893 the discovery of *Vidal black* turned the attention of manufacturers to this interesting group of colouring-matters, which now include almost all tints except red, and are obtained by fusing with sulphur or sodium sulphide, derivatives of benzene, naphthalene, diphenylamine, anthraquinone, &c. These colouring-matters are placed on the market by various firms under different names, although their compositions are practically the same: the firm of Cassella calls them *immedial colours*; the Bayer Company, *katigenic colours*; the Badische Company, *kriogenic colours*; the Berlin Aktien-Gesellschaft, *sulphur colouring-matters*, &c. The constitution of these colours has not been firmly established, but during recent years a little light has been thrown on them. According to Sandmeyer (1901) they are derivatives of **Piazthiol**,



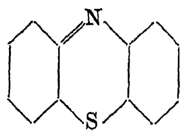
, the compound soluble in sodium sulphide having the constitution



; but nowadays other interpretations have been given.

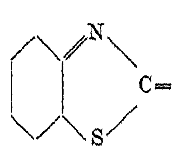
When diphenylamine-derivatives are fused with Na_2S, black colouring-matters are preferably formed, with aminohydroxydiphenylamine derivatives and the corresponding N-alkyl and N-aryl compounds blue colours are obtained, while in presence of stable metasubstituted compounds, brown or yellow colouring-matters are formed.

In general the reaction takes place with preliminary formation of aromatic mercaptans or polymercaptans (in the ortho-position with respect to N or to O), which give further condensation products, *e.g.* black derivatives of thiodiphenylamine (of *thiazine*),



,

and yellow or brown colouring-matters derived from thiazole (*see above*),



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They form insoluble condensed products (disulphides) with the oxygen of the air, these being rendered soluble again by alkaline reducing agents (sodium sulphide, hydrosulphites, &c.). The fixation and development of the colour in the cotton fibres consist simply in the oxidation of the mercaptan to disulphide. The black or blue sulphur colouring-matters are quinonimino-derivatives of the thiazine group. These colouring-matters are now used in large quantities, the production of *sulphur black* alone in 1909 being estimated at nearly 5,000,000 kilos. It has been proposed (1909) to render them faster to washing by treatment with formaldehyde or by immersion in a nickel sulphate bath.

TESTING OF COLOURING-MATTERS

Of the thousands of colouring-matters sold by different firms under most varied and fanciful names, the majority represent, not chemical individuals, but intimate mixtures of several colours which give directly the tints desired.

The colouring-matters obtained at the end of the manufacture by precipitation or separation from their solutions by means of salt (just as with soap) are not sold in the pure state, but are diluted with 50 per cent. or 75 per cent. of finely ground sodium chloride or sulphate. A *mixture* may be distinguished from a chemical individual by the following simple test: a few milligrams are blown in a cloud from a watch-glass and are caught on a moist filter-paper spread on a sheet of glass at a short distance from the watch-glass. If the filter-paper were not too moist, it shows on drying isolated, swollen points of colour, the uniformity or non-uniformity of which is readily seen. A variation of this test consists in sprinkling a little of the powder on to the surface of concentrated sulphuric acid contained in a flat porcelain capsule.

The use of the *spectroscope* has been suggested for differentiating between various groups of colouring-matters, the positions of the absorption bands being observed when white light is passed through an aqueous or alcoholic solution of the colouring-matter of definite concentration contained in a glass vessel with parallel glass walls. The spectroscope is now, however, scarcely ever used, owing to the uncertainty of the results obtained; but it is useful in detecting the colouring-matter of the blood (*see later* Hæmoglobin).

The qualitative analysis of colouring-matters for the detection of the principal groups may be carried out according to the method of A. G. Rota[1] or to those of Weingärtner and Green. The latter, which are largely used, are briefly as follow:

I. COLOURING-MATTERS SOLUBLE IN WATER. (*A*) If the aqueous solution gives a precipitate with a solution containing 10 per cent. of tannin and 10 per cent. of sodium acetate, the presence of *basic colouring-matters* is denoted:

(1) If the solution of the colouring-matter is reduced with zinc dust and dilute hydrochloric acid, a few drops of the decolorised solution are placed on a piece of filter-paper:

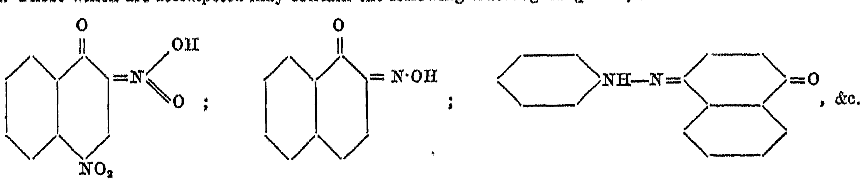
(1*a*) The reappearance of the original colour of the substance when the paper is waved

[1] Rota's method, extended by Buzzi (1911), for analysing colouring-matters consists of four series of tests:

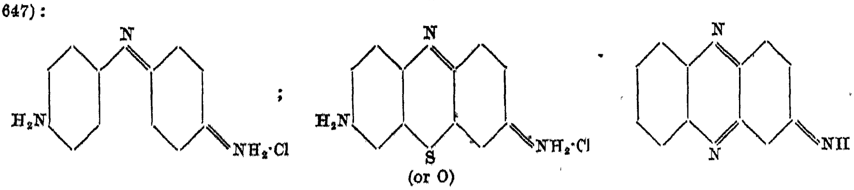
A. This is based on the usually quinonoid character of these matters and hence on their behaviour towards acid reducing agents, preferably stannous chloride; the alkaline reducing agents do not serve well, as with all colouring-matters they give leuco-derivatives which are not very characteristic.

The behaviour with $SnCl_2 + HCl$ permits of the division of all colouring-matters into the following four groups:

I. Those which are *decomposed* may contain the following chromogens (p. 647):



II. Those which are *reduced* to colourless leuco-compounds, which can be *reoxidised*, contain the chromogen (p. 647):

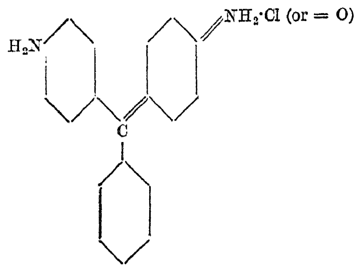


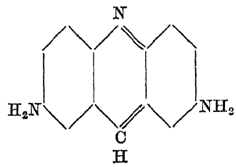
in the air indicates azines, oxazines, thiazines, and acridines, *i.e.* according to the colour, pyronine, safranine, rosinduline, phosphine, benzoflavin, indulin, &c.

(1*b*) If the original colour appears but weakly or not at all, but is formed immediately on moistening with a drop of 1 per cent. chromic acid solution, the colouring-matter belongs to the rhodamines or to the triphenylmethane group ;

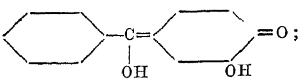
(1*c*) The non-appearance of the original colour under any conditions indicates auramine, thioflavin, chrysoidin, Janos colours, Bismarck brown.

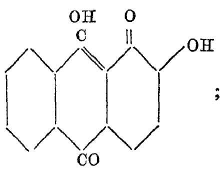
III. Colouring-matters which are neither reduced nor decomposed, but have a basic character and are partly decolorised or precipitated by caustic soda, contain the chromogens (p. 647) :





IV Those which are neither reduced nor decomposed, and have a phenolic character (feebly acid) and are increased in colour and solubility by caustic soda, contain the chromogens :





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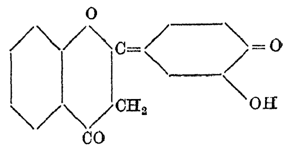
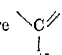


Groups III and IV always contain the chromophore  and to these belong the acridines, the thiazoles, the auramines, the rosanilines, the pyronines, the rosamines, the phthaleins, the rhodamines, the hydroxyacetones, the hydroxyanthraquinones, the coumarins, flavone, flavonal, &c.

B. To distinguish between the different chromogens of the separate groups, other special reactions are used, for instance :

The *acridines*, with concentrated sulphuric acid, give a fluorescence resembling that of petroleum.

The *azo*-dyestuffs, with concentrated nitric acid, regenerate the respective diazo-salts

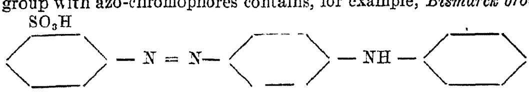
The *hydroxyacetonic*, *hydroxyquinonic*, &c., colouring-matters are precipitated as lakes by stannous chloride and subsequent treatment with sodium acetate.

The transformation of azo- colouring-matters and their derivatives into thiazole (polychromin).

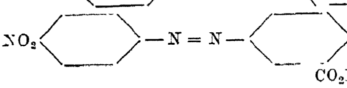
The conversion, by special reagents, of one colouring-matter into another, *e.g.* gallein into cœrulein.

C. After the restriction of the colouring-matter to one of the four groups, and after the various tests for defining more exactly the character of the chromophore have been carried out, the process of identification is continued by means of systematic dyeing tests which vary with the auxochromes and salt-forming groups (*see* p. 649), imparting to the colouring-matter a basic, acid, phenolic, substantive, or a mixed character, such as basic phenolic, acid phenolic, substantive basic, substantive phenolic.

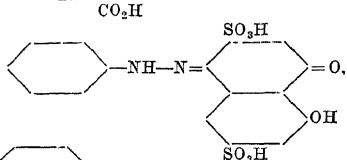
The group with azo-chromophores contains, for example, *Bismarck brown*, which is basic (*see* p. 656) ; *metanil yellow*,



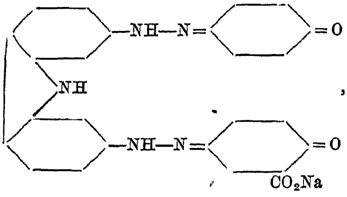
; which is acid ; *alizarin yellow R*,



which is phenolic, *Congo red* (*see* p. 657), which is substantive ; *chromotrop 2R*,



which is acid phenolic ; *carbazole yellow*,



, which is substantive-phenolic in character.

B Non-precipitation of the solution by tannin, &c (*see above*) denotes the presence of *acid colouring-matters*

(2) The solution of the colour is reduced as in (1) or with Zn + NH_3 and a drop placed on a strip of paper:

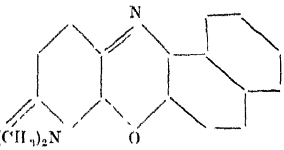
(2*a*) The reappearance of the original colour on shaking the paper in the air indicates sulphonic or mordant dyes of the groups of azines, oxazines, thiazines, soluble indulin, nigrosins or azocarmine, thiocarmine, indigo-carmine, gallocyanine, Mikado orange.

(2*b*) If the coloration reappears only after treatment with chromic acid or ammonia vapour, the original aqueous solution is acidified with sulphuric acid and shaken with ether; coloration of the ether and complete or almost complete decolorisation of the solution indicates phthaleins or auramines, while non-coloration of the ether shows triphenylmethane dyes.

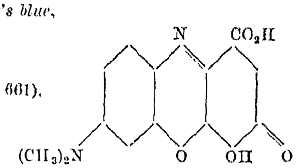
(2*c*) Non-coloration of the paper even when heated in a flame or treated with ammonia vapour points to azo-, nitro-, nitroso-, or hydrazine-colours, which, when burnt in powder directly on a platinum foil, give coloured vapours (*e.g.* naphthol yellow S, picric acid, Victoria yellow).

(2*d*) If on reduction the solution is not decolorised but becomes reddish brown and in

In the group with hydroxyazine chromophores are, for instance, *Meldola's blue*,



, which is basic, *gallocyanine* (*see* p 661),



which is basic-phenolic in character.

So, also, the thiazine group (*see* p. 661) contains *methylene blue*, which is basic, and *thiocarmine*, which is acid

The dyeing tests are made in hot neutral and acid baths, in each of which four samples are immersed, namely, cotton, cotton mordanted with tannin, wool, and wool mordanted with dichromate (for the mordanting, *see* pp 651 and 706) The more or less intense colours assumed by the samples give indications concerning the character of the colouring-matter (*see* p. 650), and confirmation of this is obtained by various tests on the dyed fabric:

(*a*) The *colour is substantive* if, when the dyed sample of natural wool is heated in faintly alkaline water, the colour passes to the white cotton placed in the same bath,

(*b*) The *colour is acid* if the change indicated in *a* is not observed, and if, when the bath is acidified, the wool takes up the colour it gave up to the alkaline bath,

(*c*) The *colour is basic* if in bath (*a*) the colour passes from the wool to a sample of white cotton mordanted with tannin,

(*d*) The *colour is phenolic* if the tint on mordanted wool varies with the nature of the mordant.

Tests may also be made on the solution of the colouring-matter, thus, if it is precipitated by tannin or picric acid, the *colour is basic*; if ether extracts the colouring-matter in an acid medium, the *colour is phenolic*, whereas if ether extracts the coloured base in an alkaline medium, the *colour is basic*.

If it is established that the colouring-matter, containing a given chromophore, is basic in nature, all acid, substantive, phenolic, &c., colouring-matters with the same chromophore are excluded.

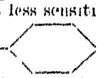
D. For the further individualisation of the colouring-matter, useful information is given by the following reactions characteristic of the substituent radicals.

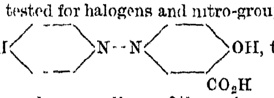
The NH_2 group is recognised by diazotising and then coupling (*see* p. 658), by which means a new azo-colouring-matter is formed, or by boiling the diazotised product with water, the formation of the OH group being shown by the increased solubility in NaOH compared with that of the original colour.

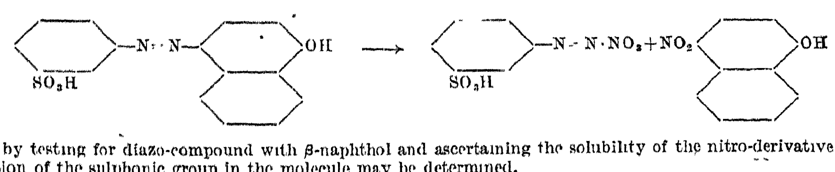
The more or less basic groups are indicated by the greater or less sensitiveness of the solution to mineral acids

The $N(CH_3)_2$ group is sensitive, as seen in methyl violet and methyl orange,

The NH_2 group is less sensitive, as in fuchsine and acid yellow;

The group —NH—  is less sensitive still, as in aniline blue and metanil yellow. Different colorations with different concentrations of acid indicate several salt-forming groups.

To complete the characterisation of a colouring-matter, the latter must be tested for halogens and nitro-groups. Thus, to distinguish alizarin yellow R (*see above*) from *diamond yellow G*,  the nitro-group is tested for by reduction and diazotisation, its presence indicating alizarin yellow. Other colouring-matters are differentiated by testing for chlorine and bromine The *azo-dyestuffs* are characterised also by the formation of the corresponding diazonium nitrates when treated with concentrated nitric acid



then by testing for diazo-compound with β-naphthol and ascertaining the solubility of the nitro-derivative, the position of the sulphonic group in the molecule may be determined.

The Tables given on pp. 674–679 afford considerable help in the rapid characterisation of colouring-matters.

RECOGNITION OF THE PRINCIPAL DYES ON FIBRES

NAME OF COLOURING-MATTER	Conc. H_2SO_4	10 per cent. H_2SO_4	Conc. HCl	HNO_3 (sp. gr. 1·40) on F [1]	10 per cent. NaOH	$SnCl_2$ + HCl
Blacks and Violets on Wool and Silk						
Indigo	F=Gn, with aq.=B s=Y, then Gn, then B	un.	un.	Y, rim Gn	un.	F=in hot somewhat D s=Gn−Y
Logwood (M. cr.)	F=Gn Br s=Y	V	R V	O and rim R	V	V then Br
„ (M. fe.)	„	„	„	Y O	„	„
Alizarin black (M. cr.)	F=almost un. s=Gr	—	F=almost un. s=r−Gr	Gn Br	+Gn B	Gn Br
Gallocyanine (M. cr.)	s=+B, with aq.=r	s=−V	F=V, s=V	R Br	F=V Gr	—
Alizarin blue S (M. cr.)	F=GnB s=+Gn B	un.	F=r B s=r	Y and rim V	F=B−Gn s=un.	V−Gr
Alizarin cyanine R (M. cr.)	F=+R B s=+B, with aq. V	+	F=+R s=−B	Gn Gr	+Gn	+Br
Alizarin cyanine brill. 3 G (M. cr.)	F=+Gn, with aq. r B s=r V	—				
Acid azo-black 3 BL (M. cr.)	R V	un.	F=−Bl−r s=r	Bl B	B	−Gn
„ „ „ (without M.)	R	−r	R Br	+R Br	+ R V	D
Naphthol black B or 3 B	F=+Gn B s=B Gn, with aq. V	almost un.	F=almost un. s=un.	R−O	almost un.	R−V
Naphthylamine black D	s=Bl B, with aq. R V	„	F=almost un. s=−Gn	Br	s=B	almost un. +V R
Anthracene black D	F=Bl V s=Gn Gr	„	F=V	Y Gn, with Br rim	s=+r	
Wool black	s=+B, with aq. V	—	F=Br V s=Br	Y with rim R	F=+V	Br Gn, then D
Victoria violet 4 B S	F=B V s=V	+R	F=R V s=r	R−O	F=Br R s=in hot D	—
Acid violet 2 B	F=Y Gr s=Y	Y Gn	F=Y Gn	Y with rim B Gn	F=almost D	+B
Acid violet 4 B N	F=Gr s=Y	+R V	Y	Y with rim −Gn	F=D	Gn B
Formyl violet 4 S B	F=Gr S=Y	+B	F=Gr s=−Y	Y	almost D	Gn
Fast acid violet 10 B	F=Gn s=Y Gr	Gn B	F=Gn, then Y s=Y Gr	Gn, with rim Y Gn		—
Alkali violet	F=O s=Y	Gn B	F=O s=Y	Y	F=D	Gn B
Violamine R	F=R s=R Gr	—	F=+B s=r	R−Y Gr	F=R	+B
Yellow Colours on Wool						
Yellow wood	F=+Y to Br R s=Y	almost un.	+Y	+Br	F=+Y s=−Y	+Y
Alizarin yellow A (M. cr.)	F=+Y, s=−Y	—	F=almost un.	Y Gn	F=+Y	—
Anthracene yellow (M. cr.)	F=Br, s=Br Gr	+Y Br	+R V	O, rim R V	F=+Y	—
Alizarin orange (M. cr.)	F=+O, s=−Br	F=almost un., s=+O	F=−O, s=Y	Y Gr	F=Y O R	almost un.
Picric acid	F=Y Gr, with aq.=Y s=with aq. −Y	F=almost un. s=−Y	F=D	Y	F=O s=Y	−Y
Naphthol yellow S	F=−Br, s=D	−Y	F=D	−Br	F=almost un., s=Y	D
Azoflavine	F=V R	+Y	F=V R, s=R V	R, rim R V	F=+Gn	−Y
Tropæolin O O	F=+V B, s=V	+Br	F=+V R, s=+V R	R, rim Br	F=+Y	+Y
Orange II	F=R Y, then R; s=R Y	—	F=R Y, then R; s=r	Y, rim R Y	F=+R Y	—
Croceine orange	F=YO, s=R	+O	F=R, s=R	—	F=Br	D
Tartrazin	F=+Y, s=Y	un.	F=+Y, s=Y	O	F=Y R, s=Y	−Y then D
Milling yellow O	F=R, with aq.=Y s=R B	+Y	F=R s=R	R, rim Br	—	D
Quinoline yellow	F=−YR, s=−Y	—	F=+Y, s=−Y	—	F=−Y	+Y
Thioflavine S	F=Br then D	−Y	F=D	—	F=−Y, then D	+Y
Green Colours on Wool						
Alizarin green (M. cr.)	F=+B, s=B	+B	F=B R, s=r	Br, rim R	F=+Gn	Gr
Diamond green (M. cr.)	F=+Gn B, s=B Gn	+Gn	F=Gn B, s=−Y	R, rim Gn	F=un.	almost un.
Janos Green C G	Gn Gr	un.	Gn	Gn B	B	Gn Y
Fast green for wool	F=YGr	—	F=+Y	Y Gn	F=+Gn	−Y
Malachite green	F=Y, with aq.=Gn s=Y	+Y	F=+O, with aq. =+Gn, s=Y	R	F=D	—
Brilliant green	F=R, with aq.=Gn s=R	−Gn	F=+Y, with aq.=Gn s=Y	R Y	F=D	+Y
Alizarin cyanine green E	Gr Gn	un.	Gr	Y Gr	almost un.	F=−Gn, s=−Y
Dark alizarin green W (M. cr.)	F=almost un., s=r	un.	F=almost un., s=r	Br	B	Br Y
Red Colours on Wool						
Brazil (red) wood (M. al.)	F=−Br R, s=Br	slowly=R	F=+R, s=R	Y, rim R	F=+R, s=R	F=R Y in hot, s=R
Sandalwood (M. cr.)	F=Br, s=Br	un.	F=Br	Br Gn	F=+Br, s=Br	F=+R, s=r
Madder (M. cr.)	F=almost un., s=R	O	F=−R, s=R	Y, rim R	F=R V	R Br
Cochineal (M. al.)	F=R Y	−R Y	F=R Y	Y	V R	R O
„ (M. sn.)	F=R V, s=R	+R	F=−R, s=R	Y	F=R, s=+R	F=+R, s=R O
Archil and cudbear	F=R Br, with aq. almost D s=R V, with aq=R	+R	F=−R s=R	Y, rim R	F=V s=V	D

Abbreviations: B=blue, Bl=black, Br=brown, D=decolorised or colourless, F=fibre, Gn=green, Gr=grey, M=mordanted, M. cr.=chrome mordanted, &c., O=orange, R=red, r=rose, s=solution, un.=unchanged, V=violet, Y=yellow, +=more or dark, −=less or faint.

NAME OF COLOURING-MATTER	Conc. H_2SO_4	10 per cent. H_2SO_4	Conc. HCl	HNO_3 (sp. gr. 1·40) on F[1]	10 per cent. NaOH	$SnCl_2$+ HCl
Alizarin S (M. cr.)	F = Br, s=−R Br	Y R	F=−Br	+Y	F=R V, s=V	R Br
Alizarin bordeaux B (M. cr.)	F=VR, s=V	—	F=Br, s=Br Gr	R Gr	F=V B, s=B	—
Cloth red B	F=+B, s=Bl B	un.	F=+V	Y, rim R V	F=R	R B
Ponceau 3 R (xylidine scarlet)	F=R B, s=R	un.	F=almost un., s=r	Y	F=O R, s=−R	slowly D
Palatine scarlet A	F=R Y, s=R B	—	F=+R, s=r	Y, rim O	F=Br R	—
Biebrich scarlet	F=Gn, s=Gn B	un.	F=Br R	R Gr	F=+B, s=V	D in hot
Croceine scarlet 3 B	F=+B, s=+B	—	F=+B, s=−B	Y, rim B	F=R V	D
Ponceau 6 R	F=V, s=V B	un.	F=R Y, s=r	Y	F=Br	—
Fast red E	F=R V, s=R V	+R	F=Br R, s=r	G, rim R Y	F=+Br R	+R
Azofuchsine G	F=V B, s=Bl V	un.	F=+R, s=r	O Y	F=−V R, s=V Gr	D
Milling red R	F=+B R, s=Br	+R	F=Br	R O	F=+R	—
Acid fuchsine	F=Y Br s=D, with aq.=r	almost un.	F=−R s=r	Y	F=D	almost un.
Azocarmine (rosindulin)	F=+Gn, s=−Gn	un.	F=+R, s=R	—	F=Br	—
Fuchsine	F=−Y Br, s=Y	F=+R B, s=D	F=Y, s=−Y	Y	F=almost D	slowly D
Eosin (yellowish)	F=O to Y Br s=Y	−Y R	F=−Y R	Y	F=+R s=r	Y O
Phloxin	F=O to Y Br	slowly D	F=Y Gr	Y	F=almost un., s=r	D
Bengal red B	F=O to Y Gr	slowly D	F=D	Y	F=+R	D
Rhodamine B	F=Y, with aq.=R +Gn	+r	F=O, with aq.=r	Y	F=r B s=D	+r
Rosindulin 2 G	+Gn	almost un.	Y Br	Y	almost un.	Br
Eosamin B	Bl B	almost un.	V	R Br	Br	+r
Chromotrop 2 R	+R	un.	−R	Y	−R Y	−R
Wool fuchsine	F=un., s=R	un.	F=un., s=r	Y	Br R	D
Acid azocarmine B	F=+B, s=Br	−V	F=R, s=R	+Y	+R	D
Fast chrome red B (M. cr. after dyeing)	F=Bl s=B, with aq.=V R	F=Br	F=Bl	F=Br Bl s=Br Y	F=+Br s=Br R	+Br
Blue Dyes on Wool						
Indigo extract	F=Gn Gr, with aq. B s=Gr	un.	F=B Gr s=−B	Y, rim Gn	Y	slowly D
Sulphocyanine G	F=Gn B, s=−B	un.	F=Gn	Br	un.	D
Alkali blue 4 B	F=+R, s= R Br	un.	F=+R, s=−Gn	Gn, rim +Gn	F=Br R	—
Carmine blue	F=−Gn to Y	+Gn	F=Gn Y to Y, s=Y +Gn B	Y, rim Gn	F=Gn, s=−B	Gn then −Y −Gn
Thiocarmine R	F=+Gn s=Gn−Gr, with aq.=B	—		Gn, rim −Gn	F=+B	
Cyanole A B	D	—	F=Gn, s=D	F=D	F=Gn, s=−Gn in hot	F in hot −Y
Methyl violet 6 B	F=O, with aq.=B s=Y, with aq.=B	B−Gn	F=O s=Y	Y	F=−V s=D	B
Crystal violet	F=O, with aq. =Gn−V, s=O, with aq.=Gn	+Gn	F=O s=Y	Y with rim +Y	F=−V	+Gn
Alizarin astrol B	F=+B, then Gn−Gr s=−r	—	F=r−B s=r−B	F=r B then Y	—	—
Victoria blue B	F=R, with aq.=B s=R	F=un. s=−Y	F=R, with aq.=B s=R	Y−Gn, rim R	F=+Br s=D	+B
Nile blue	F=R, s=Br	F=−Gn, s=−Y	F=Y−Gn, s=Y −Gn	Y−Br, rim Gn	F=+R−V	—
Indazin	F=+Gn−Gr	F=almost un. s=−R B	F=+B, s=B	Br, rim Gn	F=−R	—
Lanacyl blue B B	Gn	almost un.	R Gn	Y Br	R	almost un.
Cyanole extra	Gn, then Y	un.	Gn, then Y	Y	Gn Gr	+Gn
Alizarin saphirol B	Br Y	un.	Y Br	Gn	almost un.	almost un.
Alizarin irisol B	B Gn Gr	—	+B	D	F=−B, s=B in hot	in hot D
Wool blue R	Gn	almost un.	Y	Y Br	almost un.	+B
Eriocyanine	almost un.	almost un.	Gn Y	Y R	almost un.	almost un.
Alizarin dark acid blue S N (M. cr. after dyeing)	F=V Br, with aq =Br R	un.	F=Br s=−R	F=−Br s=V Br	F=Gr B s=−Br	almost un.
Janos blue G	Gn Y Gr	un.	+Gn	Gn B	un.	D
Carmine blue Ve (on silk)	Gn then Y Br	Gn	Gn then Y	Gn, then Y	almost un.	Gn B
Brown Dyes on Wool						
Anthracene brown (M. cr.)	F=Br R, s=Br	un.	F=Br Y, s=−Br	+O	F=Gn Br to Bl, s=D	almost un.
Anthracene acid brown B (M. cr.)	F=R V, s=R V	un.	F=+Br, s=−R V	+Br Y	F=−Br R, s=Br R	Gn Y
Alizarin brown G	B	almost un.	F=Bl, s=−Br R	F=Bl, s=Br R	R Br	Br, slowly D
Bismarck brown G G	F=R V, with aq.=Br s=Br R	F=+Br s=D	F=+Br s=R	—	F=+Br	−Br
Black Dyes on Cotton						
Diamine black R O or B O	F=+B, s=B	un.	F=−R, s=D	V	F=V R, s=r	D
Diamine black B O (developed with phenylene-diamine)	F=+B	un.	un.	—	un.	D
Diazo brilliant black B (developed with β-naphthol)	F=+B s=B	—	F=+Gn	R V	un.	Y
Columbia black R	F=+B R s=with aq. R V	almost un.	almost un.	+Br	s=−R	almost D
Pluto black G	Bl−Br	un.	V	R Br	+B	D
Vidal black	Bl Gn	un.	almost un.	s=Gr	s=GnB	Br Gr
Sulphur black 4 B extra	F=+Bl B	F=+Bl	F=+Bl	F=+Bl, s=−Gn Y	F=+Bl	F=Br Y
Immedial black Ve extra	Gr B	almost un.	almost un.	F=−Br, s=R V Br	un.	D
Zambesi black	+Gn	−Br	Br	V Br	−B	D
Aniline black	Bl Br	—	—	—	—	Bl Br, after washing=R Gr

ABBREVIATIONS: B=blue, Bl=black, Br=brown, D=decolorised or colourless, F=fibre, Gn=green, Gr=grey, M=mordanted, M. cr.=chrome mordanted, &c., O=orange, R=red, r=rose, s=solution, un.=unchanged, V=violet, Y=yellow, +=more or dark, −=less or faint.

NAME OF COLOURING-MATTER	Conc. H_2SO_4	10 per cent. H_2SO_4	Conc. HCl	HNO_3 (sp. gr. 1·40) on F[1]	10 per cent. NaOH	$SnCl_2$ + HCl
Zambesi black Ve (developed with m-phenylene-diamine)	F=Bl s=Gn Br, with aq.=Gr	F=un. s=−R	F=Bl s=−R	F=Bl s=Br	F=Bl	F=D
Indanthrene	F=Gn Br Gr, s=−Br	F=un.	F=un.	F=Y, s=−Y	F=−Gn B	un.
Diazo blue	B	un.	B Gr	R Br	almost un.	r
Oxamine blue R R R	+Gn B	almost un.	+B		V	−V
Diaminogen (developed with β-naphthol)	Bl V	un.	B	R	+B	D
Diaminogen blue B B	V B	un	F=+B, s=−B	R	F=V, s=−V	D
Benzo blue-black G	F=Gn, s=−B	un.	F=−Gn, s=D	=−R Br	F=+B, s=D	D
Diamine violet N	F=B Gn, s=−B Gn	+B	F=+B, s=D	R Br	F=+R, s=D	D
Benzo azurine G G G	F=B Gn, s=B	almost un.	F=+B, s=D	Br	F=V R, s=r	D
Brilliant azurine 5 G	F=Gn B, s=−Gn	almost un.	F=almost un.	O	F=V R, s=D	D
Benzo blue B X, 2 B, 3 B (diamine blue)	F=B Gn, s=B	B R	F=V, s=D	V R, −Br	F=V R, s=D	D
Sulphur blue L extra	F=B Bl s=B, with aq. Br	F=Bl	F=Br	F=Bl s=−R Br	F=Bl	−Y
Immedial pure blue	F=+B, s=B	F=un.	F=−B, s=B	F=V R, s=V R	F=+B, s=−B	D
Yellow Dyes on Cotton						
Auramine O	F=Y Br s=with aq. Y	−Y	F=−Y	−B	F=−Y	D
Thioflavine T	F=−R, s=D	O	F=−Y, s=Y	Br	F=un.	Br
Alizarin yellow A	Gn Y Gr	un.	−Y	Y	−Br	D
Chrysamine R	F=V R	−Y	F=V B	—	F=r	D
Diamine yellow M	F=V R, s=V	−Y	F=V R	V	F=O R, s=−r	D
Carbazole yellow	F=+B Gn, s=B	Gn Br	F=V Br, s=D	R	F=O R, s=r	D
Chrysophenin	F=V R, s=V	almost un.	F=V, s=D	V	F=un.	D
Thiazole yellow	F=−Br, s=D	O	F=O, s=D	D	F=R Y, s=D	D
Primuline	F=Y Br, s=−Y	O	F=O, s=Y	Y	F=O	Y
Primuline (developed with resorcinol)	F=R, s=R	R	F=+R, s=R	+R	F=+R	+R
Fast diamine yellow A	R	un.	Y Br	Y Br	Y R	−Y
Benzo orange R	F=B, s=B	B Gn	F=B, s=D	Br	F=R, s=Y	Br
Sulphur yellow R extra	F=−Y	—	—	−Y	—	O Y
Green Dyes on Cotton						
Italian green	+Gn	un.	+Gn	F=−Bl, s=R Br	−Gn Y	Y Br
Pyrogen green B	F=Bl	F=Bl	F=Bl	F=Bl	F=+Gn	F=−BrY
Sulphur green G extra	F=Bl	F=+Gn	F=+B Gr	F=+R	—	F=Gn, then Y Gr
Diamine green B	Bl B	un.	Bl B	V R	Bl Gn	D
Red Dyes on Cotton						
Turkey-red (alizarin with M. alum)	F=almost un. s=R Y, with aq.=Y	un.	F=O to −Y s=−Y	O	F=V s=V	in cold, almost un. in hot=D
Janos red B	Gn B	un.	B	R Br Gr	−V B	−R
Rhodamine 6 G	F=Y, with aq.=r s=Y, ,, =r	−r	F=Y O with aq.=r	F=O s=r	F=r Y s=−r	−r
Rhodamine S	F=Y, ,, =r s=Y, ,, =r	−r	F=Y O with aq.=r	R O	F=−r	−r
Fuchsine	F=−Y Br, s=Y	F=+R B, s=D	F=Y, s=−Y	Y	F=almost D	slowly D, O
Safranine	F=+Gn, s=−Gn	F=R B, s=D	F=+B, s=B	R	almost D	
Indulin scarlet	R Br	un.	Gn	B	un.	D
Congo red	F=+B, s=B	B	F=B, s=D	O	F=almost un.	D
Benzo purpurin 4 B	F=+B, s=B	+R Gr	F=+B, s=D	Y	F=almost un.	D
Diamine scarlet B	F=V B, s=V	almost un.	F=V, s=Y	R	F=O	D
Diamine red F	F=+B R, s=B	R Gr	F=V R, s=D	Br	Br	R V, then D
Thiazine red R	R Br	almost un.	R V	+R	+R	D
Brilliant geranine B	Gn B	+R	V	V	+V	D
Diamine rose G D	F=R V, s=R V	un.	F=un., s=−R V	O	−V	D
Rosanthrene B (diazotised and coupled with β-naphthol)	F=Bl s=with aq. r	F=+R	F=+R	F=−R Br	F=−R Y	F=+R
Erica B	F=R V, s=V	+r	F=+r, s=D	−R	F=−r B, s=D	slowly D
Geranine 2 B	F=−r Y, s=R	almost un.	F=almost un.	almost un.	F=V	D
p-Nitraniline red	F=R B, with aq.=R O, s=+R, with aq.=R O	un.	F=almost un.	F=R s=R Y	R Br	D
Brown Dyes on Cotton						
Janos brown	Bl Gr	un.	Bl Br	Br Gr	un.	Y Br, almost D
Benzo brown G	F=+Br, s=Gr	un.	F=+Br, s=−Br	+Br	F=almost un.	−Br
Benzo brown 5 R (terracotta F, alkali brown, brown for cotton R)	F=R s=R	almost un.	F=almost un. s=r	Br Y	F=almost un.	slowly D
Benzo black brown	F=Bl Gr, s with aq.=Br	almost un.	F=+V, with aq=Br	O R	F=+Br R	almost D
Diamine brown V	F=+BR, s=Br	un.	F=almost un.	V Gr	F=almost un.	almost D
Diamine brown R	F=Y, s=Y	—	F=Bl	F=D, s=−R	F=R (hot), s=R (hot)	V (cold), D (hot)
Diamine bronze	B	un.	R V	R Br	+Br	D
Diazo brown R extra	Bl V	un.	s=−R	R Br Gr	almost un.	−Y
Pluto brown R	V	un.	+Br	R Br	Br R	D
Thiazine brown R	R	un.	Br	R Br	Br R	−Y
Sulphur cachou R	F=almost un.	F=+Br	F=+Br, s=Br R	F=almost un.	F=−Br	un.
Immedial cachou O	F=Br Y	—	—	F=+Br	—	—
Sulphur brown G	F+Br Y, s=−Br Y	F=un.	F=−Br Y	F=Br Y, s=−Br	F=un.	F=−Br Y
Pyrogen brown M	F=+Br, s=Br	F=un.	F=un.	F=−Br, s=−Y	F=un.	F=un.

ABBREVIATIONS: B=blue, Bl=black, Br=brown, D=decolorised or colourless, F=fibre, Gn=green, Gr=grey, M=mordanted, M. cr.=chrome mordanted, &c., O=orange, R=red, r=rose, s=solution, un.=unchanged, V=violet, Y=yellow, +=more or dark, −=less or faint.

the air regains its original colour more or less, alizarin S, alizarin blue S, and the like are indicated.

(2*e*) Complete or almost complete failure of Zn + NH_3 or Zn + HCl to decolorise the solution shows thiazole yellow, mimosa, quinoline yellow S, primuline, thioflavin S, chloramine yellow, &c.

II. If the colouring-matter, in a little water and HCl, is precipitated and gives an evolution of SH_2 (detectable with lead acetate paper), and is redissolved in 10 per cent. sodium sulphide solution, the presence of a *sulphur dyestuff* is certain.

III. If the colouring-matter is insoluble in water, it is moistened and treated with a couple of drops of 5 per cent. NaOH solution:

A. If it dissolves it is reduced with zinc dust and ammonia and a paper streaked with it: (1) The rapid reappearance of the original colour in the air shows cœrulein, gallocyanine, gallein, galloflavin, alizarin blue, black, or green; (2) the non-appearance of the colour in the air indicates alizarin derivatives, alizarin itself, nitrosonaphthol, nitrosoresorcinol, Soudan brown, &c.

B. The colouring-matter does not dissolve in NaOH but is soluble in 70 per cent. alcohol: (*a*) the solution shows fluorescence, which with 33 per cent. NaOH solution either disappears (Magdala red) or does not disappear (alcohol-soluble eosin, cyanosine); (*b*) the solution is not fluorescent and is coloured reddish brown by 33 per cent. NaOH (alcohol-soluble indulin, alcohol-soluble nigrosin, alcohol-soluble aniline blue); (*c*) the solution remains fluorescent (indophenol).

C. The colouring-matter dissolves in neither NaOH nor 70 per cent. alcohol [indigo, alizarin black, sulphur colours (soluble in sodium sulphide)].

Green (1905) has shown that the different groups of colouring-matters may be characterised by their behaviour towards the compound of sodium hydrosulphite with formaldehyde.

RECOGNITION OF THE PRINCIPAL COLOURING-MATTERS ON DYED FIBRES. When the nature of a colouring-matter is to be studied, a dyeing test should always be made first (*see later*) and the tests described below carried out in the cold on the dry, dyed fabric, a small piece (about 1 sq. cm.) being treated in a porcelain dish with 1 to 2 c.c. of the reagent and any change observed. In testing with nitric acid, one or two drops of the latter are placed on the fabric and the colour of the drop and that of its edges noted. The hydrochloric acid solution of stannous chloride is prepared by dissolving 100 grms. of the latter in 100 grms. of the concentrated acid and 50 grms. of water. Abbreviations of the names of the colours and of the changes produced are used, and when a compound colour is formed, it is indicated by the two fundamental colours composing it; thus combination of red (R) and yellow (Y) gives scarlet (RY), green (Gn) and brown (Br) give olive (Gn Br), &c. (*see* Note *at foot of* Table, pp. 674 *et seq.*).

To ascertain if an *indigo dye* on wool contains also *logwood* or *sandalwood*, a piece of the fabric is heated with dilute nitric acid (1 : 6); indigo alone gives a straw-yellow, while in presence of either of the other colouring-matters, a more or less brownish colour is obtained. Or the shredded dyed textile is heated for an hour with fused phenol on the water-bath, the phenol being decanted off, the operation repeated with fresh phenol, and the material washed two or three times with strong alcohol and pressed. If the wool were dyed with pure indigo it will be quite white, but if there were threads dyed with other colours (*e.g.* anthracene blue, sandalwood, &c.) these are seen under the microscope to be still coloured.

According to E. Knecht (1909) the indigo on a cotton fabric may be *determined quantitatively* as follows: 4 grms. of the fabric, cut into pieces, are dissolved at 40° in 25 c.c. of 80 per cent. sulphuric acid; the volume is then made up to 120 c.c. with water, the indigotin of the soluble sulphate being thus precipitated. This is collected on a Gooch filter, dried at 110° to 115° and weighed. It may be redissolved in a little sulphuric acid by heating on the water-bath for an hour, the indigotinsulphonic acid in the diluted solution being titrated with permanganate. The presence of basic or sulphur colours does not interfere with the estimation, since these either remain dissolved or are decomposed. If the fabric has a coating of manganese dioxide, it must first be dissolved in bisulphite.

p-Nitraniline red may be distinguished from other reds (Turkey-red, benzo purpurin, primuline, &c.) on cotton by heating the fabric at one point over a small flame; a clear

spot is formed and part of the colour sublimes on to a piece of paper placed above the fabric. The spot does not resume its original colour either on cooling or on moistening (Knecht, 1905).

TEXTILE FIBRES

Before a description is given of the processes and plant used in dyeing textile fibres, the physico-chemical properties of these may be outlined.

WOOL. Only sheep and certain goats furnish true wool used in the great textile industries. The wool fibre is readily distinguished from the hairs of other animals by its softness and fineness and by its waviness and curling, which can be seen with the naked eye. Also under the microscope a marked difference from all other hairs is easily discernible (Figs. 424 and 425). The whole filament seems to be composed of closely superposed scales, which are more or less large according to the quality of the wool. It is the saw-like or serrated structure of these scales which explains why wool readily forms a felt when rubbed, the filaments becoming more or less firmly attached one to the other.[1]

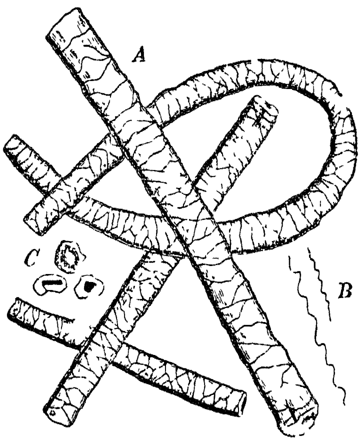


FIG. 424.

The quality of a wool is closely dependent on the breed of sheep producing it and only partially on the climate, food, and age. The yield of wool is greatest from the second to the sixth year. The finer wools, furnished generally by the *merino* breed,[2] are long, slender, soft, and very wavy and form the so-called *combing wool* for the best woollens. Shorter wools cannot be combed but only *carded* (*Silesian*, *Saxon*), although nowadays nearly all could be combed with the improved machinery available, and a large part of the carded

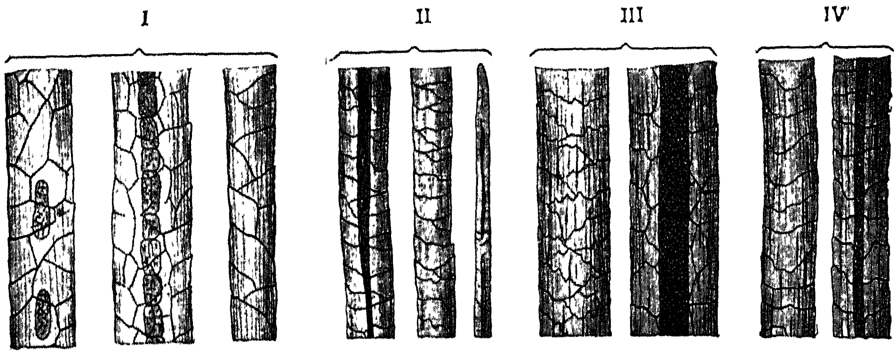


FIG. 425.

[1] The whole of the wool covering the sheep forms the *fleece*, which is kept entire even after shearing (this is done in May) owing to the scaly structure of the filaments. Wool obtained by shearing twice a year is called *bistose*, while that from slaughtered sheep is termed *skin wool* and frequently contains dead hairs, which have little affinity for colouring-matters and are often impure owing to the use of lime, arsenic, &c., as preservatives. If the sheep is washed in the tank before shearing, the wool is known as *washed*, the other being called *in grease* or *unwashed*.

The fleece (weighing 2·5 to 3 kilos) contains different parts of different qualities and these the sorters separate by cutting. In one and the same fleece the finest wool is that of the shoulders, then comes that of the neck, stomach, flanks, and back, the poorest qualities being those of the head and legs. Certain African sheep (Morocco), and, to some extent, the Lincoln, Leicester, and Wellington breeds give long, coarse, and only slightly curved fibres, which are used for special fabrics and for mattresses.

[2] *Merinos* are indigenous to the plains of Estremadura and Andalusia (Spain), where they were jealously guarded for some centuries, exportation being prevented. In the nineteenth century the Spaniards themselves introduced them into the Argentine, where three principal types were developed: *Rambouillet*, *Negrette*, and *Lincoln*, and a similar result followed the concessions made to France and Sweden. The English introduced them, with great success, into Australia and Cape Colony. The *Electoral* breed originated in merinos which were imported in 1760 into the Electorate of Hesse, and spread into Silesia, Saxony, Würtemberg, Hanover, Moravia, and Hungary; it now furnishes a large proportion of the raw material of German and Austrian wool factories.

In England the *Cheviot* breed has assumed considerable importance and yields a long, yellowish wool,

wool is obtained from *shoddy*.[1] The lengths of wool fibres vary from 4 cm to 30 cm. and the diameter from 0·014 mm. to 0·06 mm. The finer wools (merinos, Fig. 424) have as many as 13 waves per centimetre, while the more ordinary ones have only 3 (Fig. 424 *B*, natural size).

The number of sheep in different countries in 1906 was as follows (in millions): Australia, 72·8; Argentine, 74·4; Russia, 61·5, United States, 50·6; England, 29·2; New Zealand, 20·1; Uruguay, 17·9; France, 17·8; British India, 17·6; Spain, 13·3; Cape Colony, 11·8; Algeria, 9·1; Hungary, 8·1; Germany, 7·9; Italy, 11·2 (in 1908); Bulgaria, 6·9; Roumania, 5·7; Mexico, 3·4; Servia, 3·1; Austria, 2·6; Canada, 1·8, Sweden, 1·1; Norway, 1; Denmark, 0·9; Holland, 0·7; Natal, 0·6; Belgium, 0·2; Switzerland, 0·2.

The world's production of wool in 1903 was about 1,300,000 tons, namely, 450,000 in Europe, 140,000 in North America, 240,000 in South America, 2500 in Central America and the West Indies, 130,000 in Asia, 240,000 in Australia, 60,000 in Africa, and 23,000 in Oceania. For the separate countries the figures (tons) were as follow: United States, 130,000: England and Ireland, 60,000; France, 48,000; Spain, 4800; British South Africa, 47,000; Uruguay, 45,000; British India, 40,000; European Turkey and Balkan Peninsula, 30,000; Austria-Hungary, 29,000; Russia in Asia, 27,000; Germany, 23,000; Central Asia, 22,000; China, 16,000; Asiatic Turkey, 15,000; Algeria and Tunis, 14,000; Italy, 10,000; Venezuela, 7000; Portugal, 6000; Norway and Sweden, 3500; Chili, 3500; Mexico, 2300; Egypt, 1400; and Brazil, 700.

The Argentine Republic exported less than 18,000 tons in 1860, nearly 66,000 in 1870, about 98,000 in 1880, about 120,000 in 1890, and more than 200,000 (and 34,000 tons of skins) in 1895, while in 1905 the exports were about 191,000 tons of wool and 27,000 tons of skins, besides 120,000 live sheep and 3,325,000 frozen carcases.

The wool exported from Morocco in 1908 was valued at £240,000, that from Algeria in 1906 at £720,000 (£640,000 to France), and that from Tunis in 1906 at £100,000.

The great market for wool in Europe is at Antwerp, and the price is fixed by auction, account being taken of the yields of the various wools (Conditioning, *see later*) after washing, some of them losing 40 to 70 per cent of their weight owing to the removal of dirt, grease, &c.; the normal or natural moisture, after washing and drying, is taken as 18·25 per cent. The price of raw wool varies somewhat from year to year and even in the same season

not so fine as merino. *Crossbreeds*, obtained by crossing Argentines with Cheviots, are also largely bred in England.

The *Russian breeds* are derived from pure and Saxon merinos. The commonest varieties are the *ftiugsk*, *odarsk*, *rescetiovesk*, and *romanovsk* (this is used for furs). In France the wool of the Burgundy and of the Berry highly valued

Italian wools, which were once famous, are now of little importance, and only Apulia, the Tuscan marshes, and the Roman province furnish a small part of the wool consumed in Italy.

Good wool is also obtained from certain breeds of goats, such as those of *Cashmir*, which flourish in the Himalayas, nearly 5000 metres above sea-level They furnish a very fine wool mixed, however, with much white or grey hair; it is exported to France and Russia. The *Thibetan goat*, acclimatised also in France and in Bengal, likewise yields a valuable wool. The *Angora goat* of Asia Minor gives milk and a long wool (*mohair*) valued for its lustre, even after dyeing.

The *vicuna* of the Peruvian, Chilian, and Mexican mountains gives a fine wool, used in certain cloths, which are now made partly from rabbit fur (the name *vicuna* or *vigogne yarn* is also applied to fabrics of wool and cotton which are quite distinct from vicuna wool). Alpaca is greyish, and is furnished by a kind of tall, long-necked sheep (*llama*) indigenous to Peru Camel-hair, which is worked like wool, has coarse fibres, and in its natural colour is woven into certain very strong textiles used, for instance, for the seats and curtains of railway carriages.

[1] *Shoddy* is obtained by disintegrating woollen rags (previously sorted with respect to colour, and separated from those mixed with cotton) by means of an opener or *devil* formed of a drum furnished with a number of steel points and rotating rapidly inside a second, fixed drum also provided with points; from this the rags issue in short, flocculent fibres, which are carded and then spun This industry, started in England in 1845 and since then extended to other countries, allows of the utilisation of all woollen waste (fabrics and yarn), England alone imports from all parts of the world about 15,000 tons of woollen rags per annum. The coloured rags may often be partially decolorised by boiling them with 2 to 3 per cent. potassium dichromate and a little sulphuric acid Admixed cotton (sewing and other) may be eliminated from the rags by so-called *carbonisation*, which consists in immersing the rags in sulphuric acid (4° to 5° Bé), centrifuging and heating them in ovens, the temperature of which is raised to 120° to 140°. In the course of an hour the cellulose of the cotton is transformed into brittle hydrocellulose and partly carbonised, so that it can be easily removed by subsequent rubbing or by washing with water, this also carrying away the acid from the wool, which is not affected by such treatment In some cases, hydrochloric acid vapour or aluminium chloride solution is used instead of sulphuric acid The carbonised wool shows increased affinity for acid colouring-matters

Also woollen fabrics which contain bits or fibres of cotton in such quantity that it is impracticable to pick them out by hand, are carbonised with sulphuric acid or aluminium chloride before dyeing and are thoroughly washed after removal from the oven

Decolorised shoddy mixed with new wool can be recognised under the microscope owing to its different colour, which often recalls the original tint. Italy produces annually 100,000 to 120,000 quintals of shoddy.

from about 1*s.* 2*d.* to 2*s.* per kilo. Australian wool is worth more than that from the Argentine.

Unwashed wool (Australian weighs about 160 kilos per bale), after sorting, is washed with soap and soda at 45° to 50° in vessels (*Leviathans*) provided with loose forks for mixing and, when rinsed, is dried in revolving drums by means of hot air. The washed (or salted, such as Italian or Cape wool, weighing about 110 kilos per bale) wool is then carded or combed. In some districts the washing is preceded by treatment with benzene to remove the grease (*see* p. 390).

The great European market for combed wool, not yet spun but wound into balls of 4 to 5 kilos (*tops*), is in France, at Roubaix (and also at Tourcoing and Lille), where prices are fixed at auction, although there is a considerable trade in combed wool at Bradford and to a less extent at Leipzig.

These wools are classified, according to their fineness, as A, B, . . . F, the first being the finest and the last the commoner sorts ; very fine wools are marked AA or AAA.

Before being spun the washed wool is subjected to the operation of *blending*, *i.e.* the various qualities of wool (fine, ordinary, long, short, waste, shoddy, &c.) being mixed so as to obtain yarn of the desired count and fabric corresponding with the price and quality. To facilitate spinning and avoid felting, the wool is slightly oiled (with olive oil, commercial oleine, soap emulsion, &c., but not with non-saponifiable substances, such as mineral oils or resins, which would be difficult to remove from the fabric by washing, and would lead to irregular dyeing). In passing through the combs or cards, the various fibres are perfectly mixed and rendered parallel. The coarse strands (*tops*) are gradually converted into finer but not twisted strands, which are wound on bobbins (*prepared*) and are then, by means of ingenious, *self-acting* machines of enormous capacity, spun to the desired fineness to give, when twisted, yarn of the required count.[1] During spinning, the air of the room must be kept moistened with water vapour (*see* vol. i, p. 291) to prevent the parallel fibres from diverging and giving a non-uniform yarn. Satisfactory weaving also requires a certain degree of moisture.

Italy's imports and exports of wool (raw, carded, combed, spun, woven, &c.) from 1905 to 1910 were as follow:

	1905	1906	1907	1908	1909	1910
Imports, quintals	184,936	202,834	228,626	257,808	265,643	278,432 (£5,736,600)
Exports, ,,	59,164	47,996	38,862	28,348	39,351	41,697 (£1,043,500)

Woollen yarns of counts above 10 (international) pay 52*s.* per quintal on entry into Italy, while combed wool fabrics weighing less than 200 grms. per sq. metre pay £10 per quintal. The quantity of wool consumed (production + importation − exportation) in Italy was 20,160 tons in 1886 and about 28,000 in 1905.

The imports of raw wool into Japan were: 1700 tons in 1894, 9622 tons (£1,028,000) in 1904, and 10,240 tons (£1,880,000) in 1907.

Chemical Properties of Wool. Pure wool consists of C, H, O, N, and S, the last varying somewhat in amount and being partly removed by repeated washing in boiling water. It is hence improbable that wool consists of a single chemical compound (it was at one time thought to be *keratin*, containing 4 to 5 per cent. S, but there appear to be other substances also). In 1888 Richard showed that the compounds forming wool contain NH_2 and NH groups. In a solution of alkali or a salt, wool fixes chemically part of the alkali or salt. Concentrated alkali dissolves wool, forming amino-acids, the most important being *lanugic acid*, which was isolated by Knecht and Appleyard and exhibits the same behaviour towards colouring-matters as does wool.

[1] The **Count of Yarn**, either cotton or wool, is given by the number of kilometres weighing 1 kilo (international count) or half a kilo (French count). In Great Britain, the count represents the number of hanks of 840 yards (1 yard = 0 914 metre) per 1 lb (453 grms.); hence English count No. 1 is equal to French count No. 0 847 and to international count No. 1·694 Division of the international count by 1 66 gives the English count, multiplication of the French count by 2 gives the international count, while division of the English count by 1·18 gives the French count

A thread spun from two yarns of count 60 has the count 30, its weight per unit length being doubled Fine wools are spun so as to give a count of 60 to 80 or even of 120, while the commoner qualities give counts of 30 or even less.

For *silk*, the International Congress at Paris in 1900 accepted the Italian count, which expresses the weight in *denari* (one denaro = 0 05 grm.) of a length of 450 metres, the finer yarns thus having the lower counts. Silk is often spun to a count of 12 to 20 denari, and artificial silk to 60 to 120 denari.

It is probable, therefore, that wool contains at least one carboxyl group. The affinity of wool for acid colouring-matters (often sulphonic acids) is explained by the presence of amino-groups and that for basic dyes by the presence of the carboxyl group. Certain highly basic colouring-matters (such as methyl green) do not, however, colour wool, the acid character of which is too weak, while they colour silk, which is more markedly acid. The fixation of metallic oxides (of Cr, Fe, Cu, Al, &c.) in the mordanting of wool is due to the formation of salts with the carboxyl group.

The salt-forming property of wool can be easily demonstrated by immersing it in a hot colourless solution of rosaniline (base), which colours it red just as though it were dyed with red rosaniline hydrochloride. Knecht, Witt, and Nilsen have shown that the action of chlorine on wool is to intensify its acid character, so that it fixes basic dyes the more readily; at the same time it loses partially its capacity to felt.

FIG 426

Bolley found that wool decomposes potassium bitartrate in boiling solution, generating the neutral tartrate and fixing tartaric acid. In 1898 Kertesz utilised industrially, for the simultaneous production of two colours on wool, the property this shows of fixing acid colouring-matters more intensely at points where it has been carefully treated with caustic soda, the latter neutralising the carboxyl group and thus rendering the basic character more pronounced.

Wool loses much of its affinity for acid colours when treated with phosphotungstic acid, but recovers it when subjected to the action of ammonium bicarbonate (Scrida, 1909).

Of practical importance is the behaviour of wool (or cotton) waste containing ordinary oils or fats (not wool-fat), as it readily ignites owing to energetic oxidation and causes fires (*see* Pyrophoric Substances, vol. i, p. 174).

An aqueous extract of pure wool gives a precipitate with either tannin or basic lead acetate, while true glue or gelatine yields no precipitate with the latter reagent. Pure wool contains 14 per cent. N.

COTTON is the white down surrounding the black cotton-seed and is contained in capsules (each weighing about 30 grms., 10 grms. being cotton) which, to the number of 300 to 400, form the fruit of *Gossypium*—a shrub 2 to 4 metres in height (*see* Fig. 426). When the fruit is ripe (in America in August), the capsule opens and throws out a white tuft of cotton, which is fixed to the seeds. After harvesting, the cotton is freed from seeds by means of *cotton-gins* and compressed hydraulically into bales holding 180 to 200 kilos. Cotton, is produced most abundantly in North America and, to a less extent, in South America (Brazil, Peru, Colombia, &c.), and the Antilles (Haiti, Cuba, &c.). Its cultivation is also of importance in the East Indies, Syria, Macedonia, &c. Egyptian cotton (makò) is valued on account of its lustre and length of fibre. Cotton is also grown in Australia. Attempts have recently been made to cultivate it in the Italian colony of Eritrea, but without great success.

The best qualities have fibres 30 to 40 mm. in length and the lower qualities 10 to 14 mm. The fibres are 0 015 to 0·020 mm. in thickness and under the microscope have the appearance of flattened ribbons with a twist here and there (Fig. 427, the upper part of which shows the transverse sections). When treated with ammoniacal copper oxide solution, cotton swells very considerably, forming superposed capsules separated by constrictions (Fig. 428). By cold concentrated caustic soda solution (30° to 35° Bé.) the flat fibre is converted into a cylindrical one almost circular in section (Fig. 427 *l*; *see* Mercerisation) with a thin central channel. If immersion in the soda is prolonged for two or three minutes, during which the skein or fabric is kept stretched, and the soda is subsequently washed away while the tension is maintained, the skein will not contract and the fibres present a lustrous appearance (*mercerised cotton*) and are stronger and heavier than in their original state (soda-cellulose and then hydrocellulose are formed).[1]

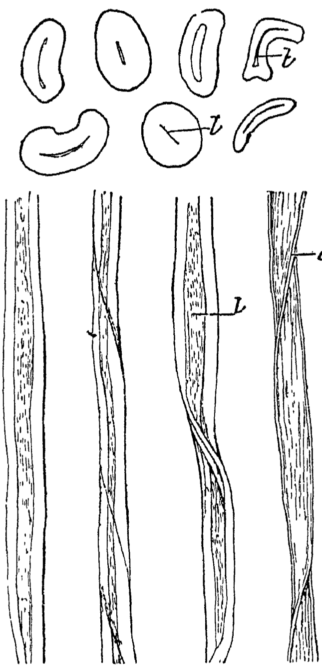


Fig 427
(Magnified 300 times)

The chemical characters of cotton are those of cellulose described on p. 503, purified cotton being pure cellulose. For its behaviour towards different dyes, *see* p. 651, and also later.

The world's production of cotton is about 3,500,000 tons per annum, about three-fifths of this quantity being given by the United States, which exports about 1,700,000 tons, nearly one-half to England, about one-quarter to Germany, and the remaining quarter to

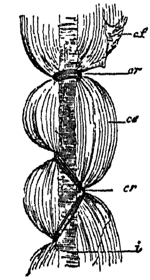


Fig. 428.
(Magnified 200 times)

[1] **History and Properties of Mercerised Cotton.** In 1844 J. Mercer, chemist in a Lancashire calico-printing works, having filtered a concentrated caustic soda solution through a cotton filter, noticed that the cloth had contracted somewhat and had become thicker and transparent. Before filtration the liquid had the sp gr 1·300, but after filtration only 1 265 On studying the phenomenon more closely, Mercer found he could reproduce it at will with yarn immersed in caustic soda solution of 20° to 30° Bé , while he established with certainty that, under such treatment, the cotton fibre shortens by 20 to 25 per cent , thickens and becomes stronger (by about 50 per cent.) and of increased affinity for colouring-matters He showed, too, that the phenomenon is more rapid and more intense at low temperatures, while at the boiling-point no contraction occurs. Similar changes are produced by treating cotton with sulphuric acid of 50° to 55° Bé. or with zinc chloride solution.

In October 1850 Mercer was granted an English patent (13,296) for increasing, by this treatment, the resistance and compactness of cotton and its affinity for dyes.

In 1884 P. and C. Depoully patented a process for the partial mercerisation of fabrics by which parts of the fabric were brought into contact with an alkali solution ; these parts contracted and caused the other parts to curl, beautiful crape effects being thus obtained.

In 1896 the textile world was astounded to see on the market samples of fine cotton of the most brilliant colours and the lustre and feel of silk. This product was prepared by the great dyeing firm Thomas and Prevost of Crefeld, according to their German Patent, No. 85,564 of March 24, 1895, which reads . ". . . . improvement in the mercerisation of vegetable fibres with alkaline or acid solutions, by subjecting the *tightly stretched* yarn or fabric to the action of alkali (caustic soda of 15° to 32° Bé.), or of acid (sulphuric acid of 49·5° to 55·5° Bé.), the stretching being maintained until washing is complete—when it is relieved spontaneously—and the shortening of the yarn or fabric thus prevented." The specification does not refer to the lustre assumed by the yarn, but this is mentioned in a later addition.

These Thomas and Prevost patents were, however, annulled a couple of years later in all countries, since various competitors found that an *identical* process had been patented (No. 4452) in England in 1890 by H. A. Löwe but had not been renewed within a year because Löwe could not find an English manufacturer disposed to make practical use of it. Large quantities of mercerised cotton are now freely produced in all countries.

The shortening of the fibre and its increase in resistance produced by concentrated alkali solution may be understood if the changes occurring in the fibre itself are followed under the microscope. While the fibre of ordinary cotton is seen to be a flattened empty tube with an occasional twist, that treated with caustic soda without stretching is shortened and swollen and forms an oval, almost round tube with thickened walls, but still with an internal channel ; outside it shows creases and a rough surface. But by mercerisation under tension, the fibre becomes like a straight, round tube, smooth and without visible creases outside and almost entirely filled up inside. These changes explain the silky lustre and also the increased strength, the fibre becoming more compact. Buntrock's experiments showed that mercerisation occurs very rapidly : with caustic soda of 30° Bé. the shortening of the fibre after one minute is 23 per cent. and after 33 minutes 29 per cent., which is the maximum attainable.

the rest of Europe) especially France, Austria, and Italy). The cotton exported from the United States in 1901 represented a value of £62,000,000.[1] Mexico produces 45,000 tons; Egypt, about 250,000; British India, 450,000; Japan, 30,000; and in the South of Italy there are about 12,000 hectares under cotton, about 5000 tons being produced. In 1899 Italy imported about 130,000 tons of cotton, mostly from the United States. The import duty in Italy is 29*d.* per quintal, yarns paying from 14*s.* to 48*s.* according to the count and fabrics 48*s.* to 104*s.*; on exported yarns and fabrics the Government grants a rebate of 3*s.* per quintal for yarns and 3*s.* 6*d.* for fabrics per quintal (freed from dressing), the weight of the cotton being increased by 8 per cent. to allow for its natural moisture.

The conversion of cotton from flock to yarn is effected by carding or combing in a similar manner to shoddy (*see above*). Very fine counts (150) are spun in some countries, but in Italy, where at one time 30 was the finest, 60 and 90 are the usual ones, although 130 is sometimes obtained.

The immense importance of the cotton industry is shown by the Table on page 687, which refers to the year 1905 (in the previous year the production was 13,635,000 bales).

In one of the cotton mills of the United States 134 workpeople are sufficient to overlook 2000 Northrop looms, a clever workman attending as many as 20 looms, while with the less expert the number never falls below 12; these looms make 165 strokes per minute with good warp and weft.

In Italy the consumption of cotton yarn and fabric amounted in 1905 to 813,000 quintals, or 2·5 kilos per head of the population. As a result of the Turko-Italian War Italy has lost the cotton trade in the Near East, which it had previously captured in competition with England and Germany.

Japan in 1903 with 4933 looms produced 69,800,000 metres of cotton fabric, the exports being valued at £720,000; in 1905 7128 looms turned out 104,500,000 metres, exports

W. Vieweg (1908) determines the *degree of mercerisation* by a method based on the fact that, in 13 to 24 per cent. NaOH solution, cotton fixes an amount of NaOH corresponding with $(C_6H_{10}O_5)_2NaOH$, while in a 40 per cent. solution it fixes double this amount, $(C_6H_{10}O_5)_22NaOH$. This soda-cellulose loses its soda when washed, and the recovered cellulose has the property of taking up more or less caustic soda in a 2 per cent. NaOH solution, non-mercerised cotton fixing 1 per cent., and mercerised 1 to 3 per cent. of NaOH according to the degree of previous mercerisation. In practice this degree of mercerisation is ascertained as follows: 3 grms. of the dry mercerised cotton are shaken for an hour with 200 c.c. of exactly 2 per cent. NaOH solution in a separating funnel, 50 c.c. of the solution being then titrated with seminormal acid and the amount of NaOH absorbed by the cotton calculated. A qualitative test for detecting mercerised cotton mixed with ordinary cotton and oxycellulose was given on p. 506. To ascertain if a fabric is mercerised H. David (1907) places a drop of concentrated soda on the fabric, which is then washed and dyed with a substantive dye, a more intense colouring on the place touched by the soda indicates that the original fabric was not mercerised.

When cotton is mercerised with tension its strength increases by 35 per cent., and when mercerised without tension by as much as 68 per cent. The elasticity is greater in cotton mercerised without tension (27 per cent.), while with cotton mercerised under tension it is unchanged (20 per cent.) The lustre of mercerised cotton is not altered by washing or dyeing.

In order to obtain satisfactory results and a good lustre by mercerising, it is best to use long-fibred cotton; the shorter the fibre the greater must be the tension. It is also necessary to boil the cotton thoroughly and wash it completely before placing it in the caustic soda bath, as otherwise, besides obtaining less lustre, there is great danger of irregular dyeing.

The dyeing is carried out in the usual way with basic dyes, being preceded by mordanting, or, better, with substantive dyes in baths containing a little Turkey-red oil or soap, the temperature being kept low at the start to avoid non-uniformity. Old caustic soda baths, which become largely converted into sodium carbonate and so diminish in activity, can be used for soap-making.

To impart a silky feel to mercerised cotton, the latter is well washed, immersed for a few minutes in a calcium acetate bath at 0 5° Bé, pressed, introduced into a bath of Marseilles soap (1 grm. per litre), again pressed, placed in an acetic or tartaric acid bath (10 grms. per litre) and finally pressed and dried without washing.

Mercerised may be distinguished from unmercerised cotton by immersion in a solution of 5 parts KI + 20 water + 2 iodine + 30 $ZnCl_2$ in 12 water. All cotton is thus coloured blue, but thorough washing with water decolorises only that which has not been mercerised (H. Lange, 1903).

[1] The increase in the production, consumption, and exportation of cotton in the United States is shown by the following figures [in 1874 the production (home consumption + exportation) was 3,500,000 bales of 500 lb.]:

	Home consumption bales	Exports bales	Imports bales
1903	3,980,567	6,290,245	—
1904	4,523,208	9,119,614	—
1905	4,877,465	6,975,494	—
1906	4,974,199	8,825,237	202,733
1907	4,493,028	7,779,508	140,869
1909	10,300,000		
1910	12,000,000		

In the United States in 1907 cotton-seeds gave also 660,000 tons of oil and 1,490,000 tons of pressed oil-cake for cattle-food. These products were partly exported—oil to the value of £3,400,000 and cake to the value of £2,320,000.

Country	Number of mills	Spindles	Looms	Workpeople	Consumption in bales of 200 to 225 kilos
England .	2207	50,964,874	704,357	550,000	3,640,000
United States, North	573	14,810,164	340,682	197,137	2,167,700
,, ,, South	659	8,050,879	174,324	120,000	2,203,406
Russia .	227	6,554,577	154,577	350,000	1,177,000
Poland .	56	1,268,547	12,000	35,000	325,000
Germany	670	8,832,016	211,818	350,000	1,761,369
France .	420	6,150,000	206,000	90,000	840,000
Austria .	130	3,280,330	110,000	100,000	650,000
Hungary	3	103,400	—	—	—
Switzerland .	68	1,711,300	17,385	19,000	100,000
Italy . .	760	2,435,000	110,000	139,000	560,000
Spain . .	257	2,614,500	68,289	—	300,000
Portugal .	15	160,000	—	—	—
Syria . . .	35	372,000	10,000	—	80,000
Norway .	9	87,832	2,293	2,635	12,000
Denmark .	3	60,000	—	—	18,000
Holland .	23	376,234	20,100	17,000	67,000
Belgium	43	1,222,138	24,000	15,000	100,000
Roumania	-	40,000	—	—	—
Turkey .	5	80,000	—	—	23,000
Greece . .		970,000	2,100	—	15,000
Asia Minor . .	4	60,000	—	—	18,000
India . .	191	5,119,121	45,337	184,779	1,744,766
China . . .	15	620,000	2,200	—	—
Japan . . .	64	1,332,000	—	68,261	900,000
Brazil . .	142	450,000	23,000	20,000	250,000
Canada . . .	22	773,538	18,267	10,000	99,000
Mexico . . .	114	628,096	20,287	26,000	140,000
Total . .	6224	119,127,146	2,117,016	2,295,120	17,511,241

being £1,360,000, and in 1907 9260 looms made 125,000,000 metres, the exportation amounting to £1,880,000.

FLAX (*Linum usitatissimum*) is a herbaceous annual, growing usually in temperate regions, and reaching a height of 60 to 80 cm. (Fig. 429). It bears clusters of blue flowers which give capsules (Fig. 430, 2) containing flattened lenticular seeds (Fig. 430, 1). It was cultivated first in Egypt, then in Greece, and later in Italy and various other parts of Europe (Belgium, Holland, Russia, &c.); in Italy the cultivation has diminished very considerably, although it is still followed in some parts and is carried on in the south of Sicily for obtaining the seeds. There are two ordinary varieties which are grown for both fibre and seed: *autumn* or *winter flax*, which has a coarse fibre and is sown in October and harvested at the end of spring, the ground being left free for another crop; and that sown in March, which is pulled in the summer when the seeds begin to brown but are not quite ripe. Flax plants are pulled by hand and arranged in sheaves to dry and to mature the seeds. After removal of the latter by threshing, the plants are made into large bundles, which are left for 15 to 20 days in stagnant water, where the action of micro-organisms (*Amylobacter*, butyric bacteria) results in the dissolution of those parts of the tissues which unite the long fibres to the cortex and to the pith. The bundles are then opened and dried in the field. Instead of being *retted* in this way, flax is in some countries heated in large autoclaves for half an hour at 125° with water from a preceding operation and then for an hour with steam at a pressure of 5 atmos. The dried flax is freed from the friable cortex by bruising between sticks, the operation being completed by blows from *scutching* knives (the waste forms the *tow*). The flax is then combed and placed on the market in large

twisted tresses of 200 to 300 grms. at 144*s*. per quintal or 80*s* to 96*s*. for short fibre. In Italy, a hectare of winter flax yields about 300 kilos of fibre and 900 kilos of seed, March flax giving 200 and 700 kilos respectively; in Ireland, Belgium, and Germany double as much fibre is obtained. The world's production is about 6,000,000 quintals, more than one-half of which is produced in Russia (where 1,000,000 hectares are under flax and two-thirds of the output is exported), while Germany produces about 450,000 quintals (importing 600,000 and exporting 250,000), Austria-Hungary 400,000, France 400,000, Belgium 250,000, North America about 200,000, Italy (from 52,000 hectares) less than 150,000 (with 100,000 spindles for flax and hemp), and England about 120,000 quintals. England, however, imports 700,000 quintals of flax (two-thirds from Russia and one-third from Holland and Belgium) to supply its 1,500,000 spindles (three-fourths in Ireland for fine yarn and one-fourth in Scotland). The cultivation of flax is falling in all countries except Russia. Thus, France had at one time 120,000 hectares under flax but now has only 20,000 (in spite of Government awards of £100,000 annually to encourage its growing), about 800,000 quintals being imported (four-fifths from Russia) to supply its 700,000 spindles, 20,000 hand looms, and 22,000 power looms. Italy has not more than 50,000 hectares under flax, and for the manufacture of fine fabrics imports annually about 40,000 quintals of fine or semi-fine flax and about 1400 quintals of undressed flax.

FIG. 429.

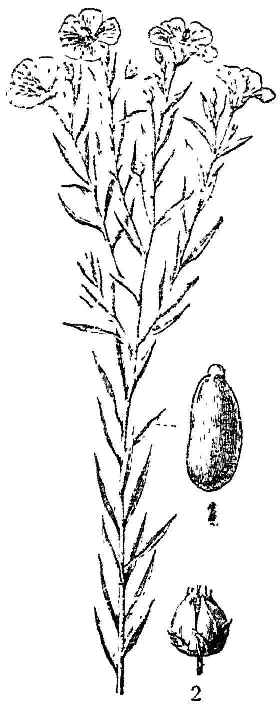


FIG. 430.

The flax fibre has a diameter of 0·02 mm. and is readily distinguishable under the microscope from other vegetable fibres (Fig. 431: 1, spiral striation; 2, extremity of the fibre and polygonal section; 3, bruised places). The fibre is spun into yarn in the same way as with cotton, but special machines are used for the recombing and repreparing of coarse fibres, which are drawn out in the moist state to a finer thread, and, at a certain stage, twisted. The tow from these operations is worked up by carding (*see* Shoddy). Flax can be spun by hand to a count of 300, but by machinery only to 200; certain qualities of flax can be hand-spun, for very fine work, to a count of 1400, such yarn costing as much as £80 per kilo.

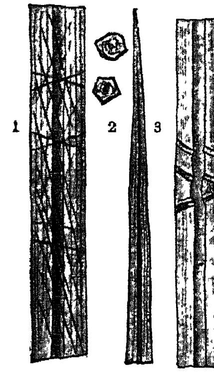


FIG. 431.
(Magnified 200 times)

HEMP (*Cannabis sativa*) belongs to the order Cannabineæ and bears male and female flowers on different plants (diœcious). When growing wild it branches (Fig. 432), but when cultivated for industrial purposes it grows to a height of 2 metres or more without branching and has a finer and closer tuft in the case of the female plants (Fig. 433). Of the different varieties of hemp (jute, Manila, New Zealand, and ordinary), the most important is the *ordinary*. It is sown very close in heavy, deeply worked soil, and is gathered in August, the plants being dried in bundles on the ground. The treatment is similar to that of flax, but with a more protracted maceration. The residue from the breaking is used to some extent in paper-making; the hemp, more or less combed, is twisted into tresses like flax and made up into bales of 150 kilos. Hemp fibres have a

diameter of 0·04–0·05 mm. and are easily distinguished microscopically rom other fibres (Fig. 435: 1, displaced fibres; 2, *a–d*, form of the tip of the fibre; 3, section of a bundle of fibres; 4, striation: the crossed transverse lines are not always seen, the parallel

FIG. 432.

FIG. 433.

FIG. 434.

longitudinal striations being more common). The long stems are cut into three lengths of about 70 cm. and are combed first by hand and then by a machine with long, coarse points, the waste forming the first and second tow, which can be subsequently carded. A third combing is carried out with finer and closer teeth, the coarse and then the finer ribbon being passed through machines similar to but coarser than those used for cotton and wool (preparing), and finally twisted for coarse twine yarn, for canvas yarn (count of 7 to 10), &c. Two twines twisted together give a *string*, several strings combined and twisted form a *rope*, and several ropes a cable.

As well as for string, rope, &c., hemp is largely used for making coarse, strong cloth for bags, waggon covers, sails, &c. In order to render hemp fabrics more compact and durable, they are sometimes mercerised.

The output of hemp in Europe is less than 4,000,000 quintals, 1,000,000 coming from Russia, 960,000 from Italy, 750,000 from Austria-Hungary, 600,000 from France, 20,000 from Belgium, and 10,000 from Holland. Italy exports nearly 40,000 quintals of string and rope, 35,000 of rough hemp and flax, and 1200 of twisted hemp and flax.

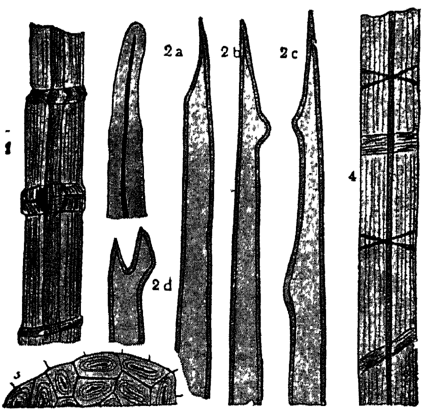


FIG. 435
(Magnified 200 times)

JUTE (*Corchorus capsularis* of the order Tiliaceæ) has been grown on an enormous scale in India and Bengal from time immemorial and is now replacing indigo. Even in 1851 India exported 282,350 quintals, and in 1858 the exports of jute sacks were valued at almost £240,000. These figures are now nearly doubled, owing to the development

of the large works in Calcutta. In Europe its cultivation was commenced subsequently to 1830. It is grown also in South America and in the United States.

Jute requires a moist, hot climate and soil It is sown in spring, and the plants, 15 to 20 cm. apart, mature in four months and attain a height of 3 to 4 metres The shape of the leaves, stem, seeds, &c., is shown in Fig. 436. It is treated in a similar manner to hemp, and the bales, weighing 180 kilos, are tightly pressed for transport. The principal European centre of the jute trade and industry is at Dundee. The jute fibre is brownish yellow, and is bleached in a faintly alkaline chloride of lime bath (5° Bé) at 25° to 30°, then rinsed, immersed in a 0.5 per cent. sulphuric acid bath for 15 minutes, and finally thoroughly washed.

FIG. 436.

Raw jute fibres are easily distinguished from other fibres under the microscope (*see* Fig 437: 1, irregular lumen of the fibre dotted at the top; 2, fibre with broken lumen, 3, tip of fibres; 4 and 5, sections of fibre with thin or thick walls) and show more or less lustre according to their fineness.

Jute competes directly with hemp since it serves for making the same articles (sacks, packing cloth, carpets, tents, furniture coverings, &c.), but when made of jute these cannot be washed.

In 1901 Italy imported 249,000 quintals of raw jute to be manufactured and 4000 of jute yarn (some again exported), and exported about 15,000 quintals of jute tissue (jute, flax, and hemp fabrics are highly protected in Italy, the duty ranging from 8*s*. to 16*s*. or even more for the finer counts and for tissues).

The consumption of jute in different countries is as follows: England, 1,280,000 bales (of 180 kilos); India, 1,200,000; United States, 540,000; Germany, 450,000; France, 260,000; Austria-Hungary, 170,000; Italy, 120,000; Belgium, 100,000, &c. Raw jute in bales costs 28*s*. to 36*s*. per quintal.

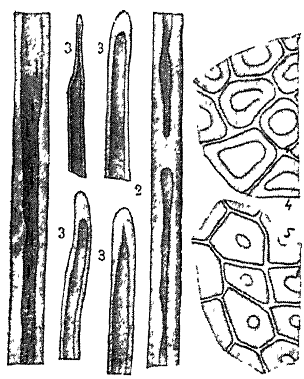


FIG 437
(Magnified 200 times)

SILK. The Chinese seem to have known the *silk-worm* as early as 2600 years B.C. Although they understood the preparation of silk materials, they did not at once trade with other races, but maintained great secrecy on the rearing of silkworms and strictly prohibited the exportation of the eggs.

According to tradition it was only in 150 B.C. that silkworms arrived in Japan, where they were imported secretly by the daughter of a Chinese emperor, and whence they spread later throughout the rest of Asia. They were apparently imported into Italy in the sixth century by three monks who hid them in their staves, although the manufacture of imported silk was begun in Italy three centuries earlier. From that time up to the present Italy has maintained the first place among the countries of Europe for the rearing of silkworms and the production of silk.[1]

[1] Silk is produced by one of the Lepidoptera, *Bombyx mori*, a larva which after birth (when it weighs about 0.5 mgrm.), feeds on mulberry leaves (*Morus alba*) and attains the height of its development (with a weight of 3 to 5 grms.) in five weeks, passing through four moults or sleeps during which it casts its skin It finally passes to brushwood arranged above, where it constructs a *cocoon* with the silky exudation secreted by two long glands filled with fibroin and leading along the body beside the intestinal canal to two very fine apertures in the mouth. The two contiguous and parallel threads thus formed are immediately stuck together by a liquid (sericin) exuded by two other channels near the first pair, the result being an apparently single thread, which is

In 1443 Florence contained 84 large silk factories and in 1580 Milan began to acquire the ascendancy, but fell back later, to advance again in the middle of the nineteenth

either white or some shade of yellow (the double thread is shown in Fig 438) In three days the silkworm is transformed into a chrysalis from which the butterfly originates (in 10 to 14 days) if the temperature is sufficiently high (15° to 30°) The butterfly emits from its mouth an alkaline liquid with which it moistens one end of the cocoon and then perforates it and issues to proceed to the coupling necessary for the preservation of the species

Immediately afterwards the female deposits numerous fertile eggs (*graine*), and both it and also the male die, their short life-cycle being at an end (Fig 439) One kilo of cocoons gives three ounces of eggs. Part of the eggs (or of the butterflies) are selected under the microscope and are kept in a cool place until the following spring, when they are hatched by incubating for a couple of weeks in an oven, the young worms being distributed to the rearing-houses In 1904 Italy exported 1521 kilos of eggs, of the value of £20,240; in 1908 9228 kilos; in 1909 2885 kilos, and in 1910 3330 kilos, worth £10,000 The imports of graine (from France) were 4178 kilos in 1906, 18,928 in 1908, 13,629 in 1909, and 5612, worth £44,880, in 1910

By means of extreme cleanliness, disinfection of the brushwood and microscopic tests of the eggs, the numerous diseases which cause havoc among silkworms at all stages (*calcino, flacherie*, &c.) have been partially overcome The crossing of different varieties has also proved beneficial, and in Lombardy the use of the Chinese cross is fairly general The silkworms from an ounce of eggs consume altogether about 12 quintals of leaves. It has been proposed to disinfect the leaves with lysoform, tachyol (ozone. Molinari, 1908), &c, but without good results.

In order that a maximum yield of good silk may be obtained, the butterfly is not allowed to issue from the cocoon, since the silk cannot subsequently be readily unwound from perforated cocoons and much waste is produced, indeed when the cocoons are placed in water (*see later*), the perforated ones become filled with water

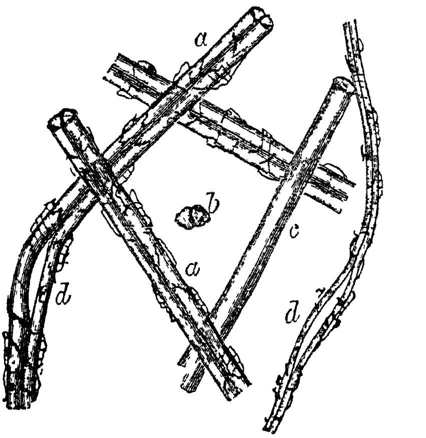


FIG 438.—*a*, double thread (*bava*) with scales, *d*; *b*, section of double thread; *c*, isolated, smooth bava, after cleansing (Magnified 120–180 times)

FIG 439.

and sink, thus breaking the thread during the unwinding The formation of the butterfly in the cocoon is prevented by *stifling* (*i e* killing) the chrysalis by heating in an oven, where the cocoon loses two-thirds of its weight. Such procedure also allows of the sale of the cocoons at the season of the year when the prices are most remunerative Ten or eleven kilos of fresh cocoons yield 4 kilos of dry cocoons, and these give 1 kilo of silk

In Japan silkworms are raised as many as three times a year. An ounce of eggs yields 50 to 60 kilos of cocoons, which are sold, freed from waste, at prices varying in different years from 2*s*. to 3*s*. 6*d*. per kilo; as waste are considered doubled cocoons (*doupions*), *stained* or *mouldy* cocoons, those attacked by calcino, and also incomplete, light, soft cocoons, and the flake silk or cover which surrounds the cocoons and attaches them to the brushwood.

The suffocated cocoons have an average weight which varies, more particularly with the variety, from 0 5 to 0 8 grm. The ratio between the weight of dead chrysalis and silk lies between 1 4 : 1 and 1 6 : 1 and the length of silk per gramme is 900 to 1500 metres, the thread (bava) varies in thickness from 0 18 to 0 30 mm.

The *cocoons* are first placed, a few at a time, in basins of almost boiling water and are rubbed with a hand-brush of twigs, to which the tangled filaments covering the cocoons become attached Among these filaments is that by which the cocoon can be completely unwound. The other filaments form the floss, which is worked up with the other waste (*see above*). Five (or more) of the threads are attached to a *reel*, which revolves rapidly and completely unwinds the cocoons. The latter float in hot water, which softens and dissolves part of the gum uniting the threads, while the remainder of the gum drys again on the reeled silk, joining the five threads to a single filament constituting raw silk As one cocoon is finished, it is replaced immediately by another so as to form a homogeneous thread. The chrysalides remaining form about 70 per cent. of the weight of the fresh cocoons and contain 22 to 26 per cent of oil (fetid); they are generally defatted and sold as nitrogenous fertiliser (for hemp, &c.) at 13*s*. or 14*s* per quintal. Cocoons which do not unwind regularly also pass into the waste.

Good cocoons give as much as 800 metres of good silk and the count of the single thread varies from 1 5 to 4 denari according to the breed of silkworm; the tenacity lies between 5 and 12 grms. and the elasticity between 80 and 150 mm.

White or greenish yellow cocoons give white or almost white (Chinese) silk and the yellow ones golden-yellow silk. The following types of silk are distinguished commercially · European, Japanese, Chinese, Canton, Bengal, *tussah* (Chinese wild silk), and Indian tussah, and of each of these there are various qualities

In the raw silk trade the variations of the count are indicated; thus, first-quality silk from 8 to 10 denari

century. In 1804 Como had only 920 looms, which increased to 2800 in 1858, while Lyons possessed 10,000 looms as early as 1685, 40,000 in 1834, and 65,000 in 1852 (present conditions are indicated later).

Raw silk consists of 60 to 70 per cent. of **Fibroin** (the fundamental constituent of pure silk) and 25 to 35 per cent. of **Sericin**, which is the gum surrounding the threads and holding them together, and can be easily eliminated with hot water and soap or, partially, with hot water alone.

Various formulæ have been attributed to fibroin: $C_{15}H_{20}O_6N_5$ (Schutzenberger), $C_{71}H_{107}O_{25}N_{24}$ (Bourgeois, 1875). From the chemico-tintorial point of view, silk has the character of an amino-acid (or of the corresponding internal anhydride), but its acid nature is more marked than that of wool. The decomposition of fibroin by means of hydrochloric acid gives glycocoll, aminopropionic acid, tyrosine, l-leucine, and other amino-acids (E. Fischer).

The formula $C_{18}H_{15}O_8N_5$ is ascribed to Sericin, which closely resembles fibroin, but gives large proportions of diamino-acids. It is thought by some that the silkworm contains only fibroin, and that at the moment when the thread is produced this is transformed superficially into sericin under the influence of air and moisture. The yellow colour of certain raw silk is due to a natural colouring-matter, **Carotin** (Dubois' hydrocarbon).

Under the microscope raw silk has the appearance of slightly flattened, cylindrical, transparent threads, not very smooth on the surface, and composed of two bave joined by the sericin (which can be distinguished from the inner part or fibroin) and thinly covered with an adhesive soluble in hot water and different from sericin, which dissolves only in hot soap solution.

In many cases the **Dyeing** of silk, especially with mordant dyestuffs, is similar to that of wool. Under all circumstances, however, the silk should be thoroughly cleaned before dyeing, and as in spinning and weaving the silk is treated with dressing (soap emulsion, vaseline oil emulsion, soluble starch, &c.) to facilitate the operations and sometimes also to increase the weight, both yarns and fabrics (even if white) are subjected to rapid cleansing

is marked $\frac{5}{10}$, first-grade tussah of 40 to 45 denari, $\frac{40}{45}$, &c). The price of tussah silk (16*s* to 24*s* per kilo) is less than half that of fine European silk, but the prices vary from year to year

With Asiatic silk it is always stated whether spun in Europe or on the spot; the latter gives much more waste in the subsequent operations.

Raw silk threads are seldom made into textiles (then called raw silk) and real silk thread is obtained by joining two or more threads of raw silk and twisting them to form the *tram silk* or *organsine* (warp) used in weaving.

To this end the raw silk is first wound on bobbins, from which it passes through felted forks—to free it from down—to other bobbins. It is then ready for twisting, which is carried out in different ways for *tram* silk and for *warp* (organsine) For the latter the best silks are used these being at once twisted from right to left, the product being known under different names according as the number of the twists per metre are 244 to 440, 440 to 488, or 488 to 610 The twisted threads are then joined in twos, threes, or fours the combined threads being twisted from left to right (or *vice versa*)—380 to 450 twists per metre for taffeta, 320 to 360 for satin, 550 to 560 for velvet, and 2200 to 3000 for Chinese crape. Before dyeing or bleaching the raw organsine is *ungummed* or *stripped* for about 30 minutes in boiling neutral soap solution (25 to 30 per cent. of soap calculated on the silk). In order to remove the gum and to obtain a maximum lustre, a second boiling soap bath is used, and finally a third. The *boiled silk* weighs about 25 per cent. less than the original organsine. When the organsine is to be dyed a pale or delicate colour, it is subjected to special treatment with sulphur or hydrogen peroxide (*see* vol 1, p 235); tussah organsine (brownish) is only bleached with hydrogen peroxide.

In preparing *tram silk* the raw threads are not immediately twisted, but are first joined in fives or tens (or more) and then twisted, but only with 80 to 125 twists per metre. The cleansing with soap is carried out at 35° and the colouring-matter is readily destroyed by immersion for 15 minutes in an aqua regia bath (2·5° to 3° Bé) at 20° to 25°, and thorough washing with water. The white tram (so-called *souple*) has lost in these operations only 5 per cent of its weight; if it is to be dyed a pale tint it is then sulphured. When a more lustrous tram is required for obtaining special effects in textile design, it is subjected to *boiling* like the organsine.

Silk Waste, including *doupions* (cocoons formed by two larvæ in the same covering; these cannot be unwound in the ordinary way), pierced cocoons, the waste from twisting (2·5 per cent in Italian and 8 per cent. in Asiatic silks), stained (mouldy) cocoons, diseased cocoons small or incomplete cocoons (from inert worms), silk tow, &c, constitutes 25 to 35 per cent. of the total crop of cocoons and often goes under the name of floss (at 4*s*. to 6*s*. per kilo; real floss costs 6*s* to 7*s*. per kilo). It is worked very similarly to cotton and to woollen rags by means of special carding and combing machines, giving first a kind of wadding and then ribbons and threads with parallel fibres. These can be converted into yarn called *chappe*, which is consumed in large quantities as it costs less than one-half as much as pure silk and for some fabrics (velvets) is a good substitute for ordinary silk. The waste from the carding and combing of chappe is also spun, giving *bourettes*. In Italy a large company with seven works enjoys a kind of monopoly in this trade: they work up foreign waste and part of the native waste, the Italian Government imposing a small export duty which acts detrimentally against the spinners and forms a protective duty on foreign waste yarn.

The value of the raw waste worked up in Italy is about £1,000,000, its subsequent value being about £1,600,000 (*see also* Statistics).

with hot soap solution (80° to 85°) containing a little sodium carbonate, and are then well rinsed in tepid water.[1] If the wares are to remain white, they are sulphured (*see* Note) or treated with hydrogen peroxide solution, the characteristic rustle (*scroop* or *crackle*) of silk being imparted by immersion in a 1 to 2 per cent. sulphuric or acetic acid bath, centrifugation and drying without rinsing.

Dyeing is in general carried out in soap baths, using one-third or one-fourth of the soap solution remaining after the boiling of the raw silk, acidifying it with sulphuric acid, boiling and agitating. The silk is immersed in this emulsion for a time and then removed, the bath being diluted with water and the colouring-matter (acid or basic); the dyeing is begun at 35° to 40°, the temperature being gradually raised almost to the boiling-point. Acid colouring-matters are fixed by silk also from a hot acidified aqueous solution, but the tints are not so lasting.

The dyed silk is rinsed in water and transferred to the acid bath to obtain the *crackle*, which becomes more pronounced as the acidity and temperature of the bath are raised, but the acid remaining in the dry fibre slowly attacks it, with injury to its tenacity and elasticity.

Nowadays silk is usually *weighted*, *i.e.* impregnated with various substances (organic and inorganic), in order to increase its weight (by 30 to 40 per cent. and sometimes, with black silk, even by 300 per cent. or more). Silk possesses, indeed, the property of absorbing from solution large quantities of tannin; this can be fixed by means of salts, and fresh tannin can then be absorbed, and so on. Successive amounts of insoluble metallic salts (tin salts, phosphates, silicates, &c.) may also be precipitated on silk. To weight white silk, the boiled silk is soaked for an hour in a stannic chloride bath of 25° to 30° Bé. [at one time **pink salt**, $SnCl_4,2NH_4Cl$ (*see* vol. i, p. 609) was largely used, but at the present time, crystallised tin salt, $SnCl_4,5H_2O$, is mostly employed], manipulated for 30 to 40 minutes in a hot disodium phosphate bath (4° to 5° Bé.), washed slightly with water, introduced into a sodium silicate bath (3° to 4° Bé.) and again washed. Treatment with this series of baths (stannic chloride, phosphate, and silicate) is repeated several times, according to the degree of weighting desired; five such repetitions give a weighting of 100 to 120 per cent. (the weight being doubled).[2] Weighted silk can be dyed, and in the preparation

[1] It is generally necessary to ascertain, before dyeing, what will be the loss in weight of the silk during ungumming or stripping. White Italian silk loses on an average 21 5 per cent.; Japanese, 20 per cent; Canton and Chinese, 24 per cent, raw yellow Italian, 24 per cent, and chappe, 4 per cent. The loss, which includes also any weighting of the yarn with vaseline, soap, oils, glycerine, &c, is determined as follows 50 grms of the silk are manipulated in a solution of 15 grms of seasoned Marseilles soap of good quality in a litre of hot water, which is allowed to boil gently for half an hour, and are then removed, pressed or centrifuged, boiled for a further period of 30 minutes in a soap bath similar to the first, and washed thoroughly with water until the latter remains clear; after being centrifuged, the silk is dried in an oven until of constant weight. The loss of weight on stripping is referred to 100 grms. of dry silk, so that allowance should be made for the *normal humidity* (11 per cent.) of silk.

[2] The phenomenon of *weighting* is explained, according to Sisley (1911), by regarding silk as a *colloid* (*see* vol. i, p. 102), which absorbs hydrogels (*e.g.* stannic) of various salts of polybasic acids But many substances which give precipitates and insoluble salts do not serve for weighting, since they are not firmly retained by the silk fibre —and are therefore eliminated during washing and dyeing—and are not dyed. The weightings which have given the best results in practice are: (1) tin hydroxide (used as early as 1869 in a Lyons dyeworks), (2) tin phosphate; (3) tin silicophosphate; (4) tin and aluminium silicophosphates. Sisley (1896) showed, and Franckel and Fasal (1897) and Severini (1906) confirmed, that weighting is due purely to a physical and not to a chemical phenomenon, since the weighting bath undergoes no chemical change and no alteration in concentration. Further, when silk soaked in stannic chloride is washed with water, the precipitated stannic hydroxide which is formed in abundance as a result of hydrolysis is not fixed by the silk and is derived from the chloride on the surface of the thread, that *absorbed* inside the fibre remaining as a kind of colloidal solution of stannic hydroxide in hydrochloric acid, the acid diffuses into the fibre, which retains it, whilst the stannic hydroxide is fixed as a gel and does not influence the feel and lustre of the silk. The absorption of stannic chloride is avoided if the silk is previously treated with tannin. In 12 hours silk which has absorbed 11 per cent. of tannin fixes from a stannic chloride bath of 30° Bé, only 1 25 per cent of SnO_2, while silk without tannin fixes about 12 per cent. of SnO_2 from the same bath; these different silks also take up varying quantities of colouring-matters When washed, the stannic hydroxide formed on the fibre is $Sn(OH)_4$ or $SnO_2,2H_2O$, retaining small amounts of HCl; the washed silk is therefore introduced into a bath of sodium carbonate, which forms a labile compound of Na_2CO_3 and $SnO_2,2H_2O$, this being decomposed by acid with formation of a tin hydroxide insoluble in acid and in subsequent stannic chloride baths.

Boiling or treatment with a soap bath of washed silk containing $SnO_2,2H_2O$ results in the separation, in a firmly fixed condition, of the hydrate Sn_4O_2,H_2O, *i.e.* $Sn_4O(OH)_2$, which has, however, but little affinity for phosphates and silicates (Gianoli, 1907). Weighting with stannic chloride gives a regular increase of 10 to 12 per cent. in the weight for each separate operation on the same silk. In weighting with tin phosphate (after the chloride bath, the silk is passed into a hot disodium phosphate bath and then washed thoroughly with water, the operation being repeated if necessary), the first operation gives an increase of about 20 per cent., but subsequent operations produce larger increases; the third may give as much as 35 per cent. Silk alone has no affinity for salts of polybasic acids (phosphoric, tungstic, &c), but if it is first passed into a tin salt bath it fixes them, for example, as SnO_2,Na_2WO_4 or SnO_2,Na_2HPO_4 (sodium phosphostannate, insoluble in water but soluble in concentrated sodium phosphate solution); only phosphates containing hydroxyl groups are fixed by tin, so that trisodium phosphate

of black silk, the weighting may be increased considerably by passing the weighted white silk (washed with a little soda) into a cold bath of ferrugine (a slightly acid solution of basic ferric sulphate prepared by heating a solution of ferrous sulphate with sulphuric and nitric acids), slightly washing the silk thus coated with oxide of iron and immersing it in a bath of potassium ferrocyanide (acidified with HCl) which colours it blue. It is then placed in an almost boiling tannin bath (*e.g.* chestnut extract), next in a tin bath to fix the tannin, and finally in a hot bath of logwood extract to obtain an intense *black tint*; the dyed silk is rinsed in soap solution or an acidified oily emulsion, livened in a sulphuric acid bath, centrifuged and dried. By repeating the tannin and metallic baths ten or fifteen times, weighting of 300 to 400 per cent. may be obtained. Black silk weighted to the extent of 400 per cent. and partly attacked shows under the microscope a heavy incrustation round the fibre (Fig. 440); much of its resistance has been destroyed, and under the action of sunlight it undergoes rapid corrosion (umbrellas of heavily weighted black silk split even without using). O. Meister at Zurich (1902) and independently G. Gianoli at Milan (1904; Ger. Pat. 163,622) found that this inconvenience can be largely avoided by means of a thiocyanate bath. In 1906 the Società della stagionatura della seta di Milano (as a result of investigations of Sisley at Lyons and of Gianoli and Colombo) filed a patent in America for the preservation of weighted silk by introducing it in a bath of thiourea faintly acidified with citric acid; U.S. Pat. 873,902, was granted in February 1908, and appears to give excellent results in practice.[1] O. Meister (1910) suggests the use

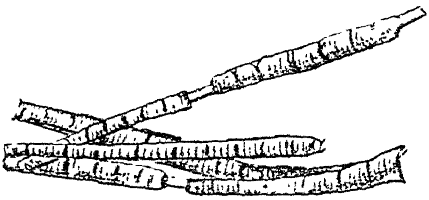


FIG 440.

and sodium pyrophosphate are not fixed If the sodium carbonate bath follows the chloride bath, less sodium phosphate is subsequently fixed. Treatment of the silk in the acid bath results in the removal of the whole or a good part of the sodium. When the silk has been treated in the first sodium phosphostannate bath, it is washed and introduced a second time into the stannic chloride bath, the double decomposition thus produced resulting in the formation of insoluble phosphate of tin, which is fixed on the fibre, and of sodium chloride, which passes into the bath, while at the same time the silk becomes impregnated anew with $SnCl_4$—this fixing tin hydroxide on the fibre when the latter is washed. This tin hydroxide gives fresh sodium phosphostannate when introduced into a second disodium phosphate bath, while the bath, which becomes impoverished in soda, continually increases in acidity and the weighting of the silk increases during successive operations.

Still higher weighting is obtained if the sodium phosphostannate silk is introduced into one or several more or less concentrated and more or less hot sodium silicate baths By this means part of the phosphate residue united to the tin oxide is replaced by silica, the compound $3SiO_2 Na_2O,SnO_2$, being formed, the silicate bath becomes acid and contains trisodium phosphate. In the acid bath, this silk readily loses sodium, being formed of insoluble tin trisilicate. This weighting was patented by Neuhaus in 1893, but had been previously used in France

The highest weighting of silk is obtained by following repeated phosphate baths with a bath of an alum salt, as was proposed by Puller (Crefeld) (Fr. Pat 254,659 of 1906) In this way the aluminium is fixed as phosphate and a little sodium passes into solution After washing, this silk is passed into a sodium silicate bath and has the property of fixing much more silica than in the case described by Neuhaus; further the silk loses practically nothing in the acid bath, since the sodium of the tin silicophosphate has been replaced by aluminium Nicolle and Sisley (1911) found that various other salts may be used in place of those of aluminium, but that only those of zinc gave good results in practice

This general theory of Sisley on the phenomenon of weighting of silk is not universally accepted P Heermann (1904–1911) holds that while the silk is immersed in the stannic chloride bath the latter diminishes in concentration, and part of the tin remains fixed even when the silk is washed with water; he also regards the formulæ of the salts fixed on the silk as different from those given by Sisley

[1] In *determining the weighting of silk* 2 grms. are boiled for two hours in a soap bath (30 grms. soap per litre) and then for at least an hour (to expel the ammonia) in a sodium carbonate bath at 1 5° Bé, the water evaporated being gradually replaced. It is then rinsed well with water and dried and the nitrogen in 0 6 to 0 8 grm. determined (as was suggested by St. Claire Deville in 1878) by Kjeldahl's method (*see* p. 10), from this the quantity of true fibroin can be determined, knowing that 5 455 parts of fibroin correspond with 1 part of nitrogen With black silk containing cyanide (Prussian blue), the latter must be previously eliminated In order that the fibroin may be acted on as little as possible, P Sisley (1907) separates it as follows: 2 grms of the fabric are boiled for 10 minutes in 25 per cent. acetic acid, washed, heated for 10 minutes at 50° in a 3 per cent sodium phosphate ($Na_3PO_4,12H_2O$) solution, washed again, and boiled for 20 minutes in a bath containing 3 per cent of soap and 0 2 per cent of soda, this procedure is repeated, the tissue being washed and dried and its nitrogen-content determined The percentage weighting p (the increase in weight of the original silk) is given by $p = 100(g - c)/c$, where g indicates the weight of the dyed silk while c represents that of the raw silk (*i e.* fibroin + sericin + 11 per cent moisture) or fibroin + normal loss on stripping (21·5 or 24 per cent; *see* preceding Note). A silk is said to be weighted 50 per cent when 1000 grms. of raw silk give 1500 grms. of dyed silk.

During recent years, another simple method has been used for determining the ordinary tin silicophosphate weighting: 2 grms of weighted silk of known moisture content (*e.g.* 10 per cent.) are treated for an hour in a platinum dish with 100 c c. of a cold aqueous 2 per cent. hydrofluoric acid solution; the latter is poured away and another 100 c.c of the acid added and left in contact with the silk for an hour. The silk is washed seven times with successive amounts of 150 c c of water, pressed, and dried at 100° to 105° until of constant weight. If the latter is 0 95, then 2 grms of moist silk = 1 8 grm dry silk, and 1·8 − 0 95 = 0 85 (weighting) So that if the

of formaldehyde bisulphite (1 to 5 per cent. bath) to check this corrosion, while Berg and Janhoff (1911) prefer the use of hydroxylamine. The use of a *diastofor* bath (*see* p. 500) after dyeing has also been proposed. Silk weighted with $ZnCl_2$ is preserved in a thiosulphate bath (Herzig, 1908).

STATISTICS. An idea of the importance of the Italian silk industry is given by the fact that silk always makes up more than one-third of the value of the total exports: £12,760,000 out of £41,040,000 in 1894; £20,800,000 of £57,240,000 in 1899, and £24,680,000 of £69,240,000 in 1905.

The production of *cocoons* in Italy during the past ten years—with the exception of the scarce crop of about 45,000,000 kilos in 1903—averages 55,000,000 to 60,000,000 of kilos, weighed alive (from 1 200,000 ounces of silkworms); in 1908 the crop was 52,000,000, in 1909 50,000,000, in 1910 44,000,000, and in 1911 about 39,000,000 of kilos, although the inaccurate official statistics give much lower values. About 38 per cent. of the crop is yielded by Lombardy, 19 per cent. by Piedmont, 21 per cent. by Venice, 7 per cent. by Emilia, 5 per cent by Marches and Umbria, 5 per cent. by Tuscany and Latium, and 5 per cent. by Southern Italy and the Italian Islands The price per kilo of fresh cocoons, according to returns from Milan, has shown the following fluctuations, depending partly on the size of the crop. 1892, 33*d.*; 1893, 38·5*d.*, 1895, 29·5*d.*; 1896–1898, about 23*d.*; 1899, 34*d.*; 1900–1902, about 28*d*, 1903, 36 5*d.*, 1904, 24*d.*; 1905–1906, 32*d.*; 1907, 39*d.*

In Japan two or three crops of cocoons are gathered per annum (*bivoltine* or *trivoltine* worms), 59 000,000 kilos in the spring, 13,250,000 in summer, and nearly 20,000,000 in the autumn. The production of cocoons in 1909 was 900,000 kilos in Spain and 8,546,536 in France (same in 1908, and 5,110,000 in 1911).

Japan also produces a considerable amount of green wild silk—of *Bombyx yamamai*, which feeds on chestnut and oak leaves (the wild silkworm of India eats castor oil leaves).

The world's production of *raw silk* (excluding the local consumption of the Far East, this being valued at about 55,000 quintals for China and 47,000 for Japan, in 1906, and about one-third more in 1907) is shown in quintals by the following Table (the value of raw Italian silk is taken as 32*s.* to 36*s.* per kilo):

Locality	Average for the years						
	1881–1885	1886–1890	1891–1895	1896–1900	1901–1905	1906	1909
Italy	27,600	33,110	44,280	42,150	43,260	47,450	42,500
France	6,310	6,920	7,470	6,500	5,910	6,050	6,740
Spain	860	720	860	830	800	560	800
Austria-Hungary	1,530	2,650	2,570	2,720	3,150	3,420	3,800
Anatolia (Brusa)	1,400	1,860	2,650	4,020	5,180	5,540	
Syria and Cyprus	2,350	3,030	4,000	4,560	4,870	4,700	15,700
Salonica, Adrianople	1,010	1 340	2,000	1,620	2,350	2,570	
Balkan States	—	—	120	470	1,410	1,850	3,150
Greece and Crete	18	21	380	410	640	750	700
Caucasia	—	—	—	2,760	3 910	4,550	5.400
Turkestan	2,050	91	1,920	1,680	4,680	6,280	
China, exported from Shanghai	24,180	27,570	10,300	45,080	42,270	42,620	
China, exported from Canton	8,910	1,277	13,730	20,210	21,280	19,620	157,200
Japan, exported from Yokohama	13,000	20,560	33,006	34,590	48,650	59,920	
India, exported from Calcutta and Bombay	4,060	4,360	261	2,930	2,560	325	
World's total, quintals	94,380	116,000	152,950	170,530	190 920	209,130	242 000

raw silk is calculated to lose 24 per cent on stripping, the weighting will be $0{\cdot}95 : 0{\cdot}85 = 76 : x$ (76 is the percentage of silk remaining after stripping) and $x = 68$, hence the dyed dry silk contains 76 parts of dry stripped silk (or 100 of raw silk) and 68 of weighting, total 144 The silk was hence weighted 44 per cent Gianoli and Colomba (1907) showed, however, that in some cases when metastannic acid is formed on the fibre, *e g* by the fixation of tin salts with sodium carbonate, the whole of the weighting is not eliminated by hydrofluoric acid, even when this is followed by a bath of HCl. A more certain result is then obtained by the old method (*see above*) or by using first soda and then potassium hydrogen oxalate P Hermann (1909) proposes to modify the alternate treatment with hydrochloric acid and caustic potash (Ristenpart, 1908) of black on tin salt and catechu, by replacing the caustic potash with a solution of normal caustic potash and concentrated glycerine (28° Bé) in equal parts, the latter preserving the silk, readily dissolving Prussian blue (by treatment for an hour in the cold or 10 minutes at 80°), but leaving the oxide and tannate of iron unchanged.

The world's production was 18 millions of kilos in 1903 ; 20·5 in 1904 ; 18·5 in 1905 ; 21 in 1906 ; 22 in 1907 ; 24 in 1908 ; and, in spite of diminished European production, 24·2 in 1909 (15·7 from the Far East, 3·1 from the Levant, and 5·4 from Europe).

In China the exportation of real silk tends to diminish, but that of *wild silk* (or *tussah*) increases ; this is produced by *Anterea mylitta* and is readily recognised under the microscope (Fig. 441). China exported 1,260,000 kilos in 1900 ; 1,325,000 in 1903, and 2,000,000 in 1904.

To the quantity of raw silk produced in Italy from home-grown cocoons must be added that obtained from cocoons imported from abroad, viz. 3000 quintals in 1893 ; 7320 in 1898 ; 11,000 in 1903, and 13,000 in 1906. The mean annual importation from 1901 to 1905 of cocoons (calculated dry) was 37,736 quintals (46,000 in 1906) with a mean yield of 1 kilo of silk per 4 kilos of dry cocoons (at 7*s.* to 9*s.* 6*d.* per kilo) or per 11·5 kilos of fresh cocoons.

To the 60,000 quintals of raw silk yarn produced in Italy must be added 24,000 quintals of silk simply treated and imported from the Far East to be spun and twisted. But only about 10,000 quintals are woven in Italy, the rest being exported (50,000 quintals of raw silk and 39,000 of twisted).

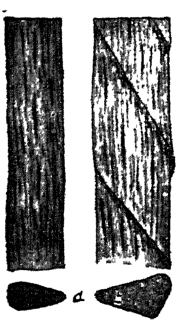


FIG. 441.

It is estimated that in 1903 there were more than 61,000 *basins* (against 54,000 in 1891) ; about 95,000 operatives for treating the silk (100 basins require 10 to 12 quintals of fuel per day) ; more than 1,667,000 spindles (against 1,500,000 in 1891) with 54,000 workpeople ; and 20,000 looms (of which one-half are power-looms running at 100 to 160 picks per minute, and the remainder hand-looms at 50 to 60 per minute) with 30,000 workpeople (against 10,000 looms in 1891), almost all of these being in the province of Como and neighbouring districts. Eighty per cent. of the workpeople are women.

The Italian weaving industry is capable of considerable extension, its produce being valued at only £3,200,000, while Switzerland [1] (with 35,000 looms) produces silk fabrics to the value of £5,600,000, France [2] (with 140,000 looms) £19,600,000 ; England about £13,600,000 (importing £8,800,000) with 87,000 looms, and about the same for Germany. If Italy were to weave the £8,000,000 worth of yarn which it exports, the value would be increased to £16,000,000 (a kilo of fabric costs about double as much as a kilo of yarn) while 200,000 more workpeople would be employed.

Mention has been made of the silk waste industry in Italy on p. 692.

During the past twenty-five years the silk-weaving industry has become of considerable

[1] Switzerland has two very important centres at Zurich and Basle, where the output of silk goods is continually increasing, although the production of cocoons is gradually diminishing. In the canton of Ticino, where the silkworm is reared, the cocoons produced have diminished from 187,500 kilos in 1872 to 58,000 in 1904, while there has been a corresponding increase in the importation of raw silk from China, Japan, and Italy This importation rose from 514,400 kilos in 1893 to 637,000 (worth £960,000) in 1902, but about one-third of this, after being twisted in the Swiss factories, is exported to Germany, Russia, and Italy. In the canton of Zurich alone in 1900 there were at work about 21,000 hand-looms and 13,330 power-looms for silk and mixed silk fabrics.

The Swiss exports of pure silk tissues in 1893 were 966,700 kilos (£2,506,100), those of mixed tissues being valued at £580,000. In 1903 the exports of silk fabrics were 1,760,300 kilos, worth £3,780,000, while the total imports in the same year were 149,000 kilos (£330,800) of silk fabrics and also mixed fabrics to the value of £112,000. One-half of the exports goes to England. The silk ribbon and embroidery industry of Switzerland is steadily advancing.

Germany is a large importer of raw silk (about 3,000,000 kilos, largely Italian), and, besides supplying home demands, exports considerable quantities of manufactured goods (*see* Table *later*).

Russia consumes about 1,500,000 kilos of raw silk annually.

[2] None the less interesting is the condition of affairs in France, although the production of fresh cocoons is only 8,000,000 kilos (1905). The imports of raw silk are calculated to be about 9,000,000 kilos, and the silk industry (almost entirely concentrated in the city of Lyons) occupies one of the foremost positions among French industries. The province of Lyons contains more than 25,000 power-looms for silk-weaving, in addition to a larger number of hand-looms. In order to reduce the importation of raw silk and increase that of cocoons, and so encourage the direct spinning of the latter, the French Government in 1892 offered a premium of £16 for every new four-threaded basin established, but the results did not come up to expectations.

While in 1893 the production of silk goods was valued at £15,150,000, in 1902 it reached £17,800,000. The French exportation of silk wares of all kinds amounted in 1896 to 4,220,000 kilos, worth about £10,000,000, while in 1904 it rose to 5,700,000 kilos, of the value of £13,200,000 (including about £1,200,000 worth despatched by parcel post).

The value of the products woven in Lyons in 1904 was £16,360,000, in 1905 £15,640,000, and in 1906 £17,040,000. In the department of Saint-Étienne the output of silk *ribbon* in 1906 was valued at £3,760,000, one-third of it for export.

The French home consumption of silk wares is about 4,000,000 kilos, this large amount helping considerably to maintain the silk industry in an active condition.

importance in the United States, where raw silk is almost free from customs duty, while the manufactured products (yarn and fabric) are very heavily taxed. These conditions have led to the rapid development of American spinning and weaving.[1] The importation of raw silk into the United States shows continuous and rapid increase, the annual averages being: 1881–1885, 15,300 quintals; 1886–1890, 23,100; 1891–1895, 31,300; 1896–1900, 43,500; 1901–1905, 65,300 quintals, which is about one-third of the world's production (excluding the local consumption of the Far East).

The Italian silk industry has passed through various crises, not on account of excessive production—since working on stock is not usual with silk articles and the demand is often greater than the supply—but owing to various circumstances, not the least among which are the tariffs raised against Italy as retaliation for the protection of many Italian industries by the tariff of July 1887. The most acute crises of the Italian silk industry were those of 1893 and 1903, which were the cause of numerous financial disasters, and that of 1907–1908, the effects of which are still felt, and which resulted from the great American crisis and is now being aggravated by French and Japanese competition. The quinquennial average price of raw Italian silk fell gradually from 62·1*s.* per kilo in 1876–1880 to 38·1*s.* in 1901–1905, mainly owing to increase in the world's production (*see* Table, p. 695). In 1906 and 1907 a rise in price of raw silk occurred; thus, that of organsine sublime (count $\frac{18}{20}$) was 40*s.* per kilo at the end of 1905, and rose to 49*s.* 6*d.* towards the end of 1906 and to 60*s.* 6*d.* in August 1907, after which a fall took place owing to the American crisis.

Silk-twisting in Italy in 1910 employed 800,000 spindles (four-fifths in Lombardy and the remainder in Piedmont), which produced 4,500,000 kilos of organsine and tram, about one-half from imported raw silk.

The *silk-waste* which was produced in Italy in 1910 (and was exported to the extent of two-fifths while the remainder was worked up in Italy) amounted altogether to 5,300,000 kilos of the value of £500,000.

Silk, carded and combed in Italy, amounts to about 1,500,000 kilos and the chappe yarn to almost 900,000 kilos, of which 200,000 kilos are consumed in Italy and the rest exported. Six thousand workpeople are employed in the treatment of waste, the ten establishments in this trade containing about 80,000 spindles in 1912.

The exportation of fabrics from Italy was 288,428 kilos in 1892; 443,371 in 1895; 1,011,567 in 1900; 1,254,416 in 1905; and 1,304,750 in 1908.

The countries with large outputs of cocoons are not always large consumers of silk wares, while in general large consumers are not producers. Italy has a total internal consumption of 6500 to 7500 quintals of silk articles, and the relation between home consumption and exportation for the principal countries in 1899 was as follows:

	Home consumption Per cent.	Exports Per cent.		Home consumption Per cent	Exports Per cent.
France	61	39	Switzerland	5	95
Germany	60	40	United States	95–100	0–5
Austria	88·5	12·5	China	about 50	about 50
Italy	20	80	Japan	„ 50	„ 50

As regards the quantity of raw silk passing through their conditioning establishments, the two principal silk markets in the world are Lyons and Milan, which together receive

[1] The protective duty on manufactured wares was 50 per cent. ad valorem in 1883, while it rose to 75 per cent. in 1897, and later to 90 per cent In 1882 there were only 8000 power-looms (including 2500 for ribbon) and 3100 hand-looms for silk in the United States, while in 1901 the number of power-looms was 52,000 (7000 for ribbon) and that of hand-looms was reduced to 800 In the same period the number of spindles for twisting and spinning increased from 450,000 to 1,900,000. The output of silk gloves was 2000 dozens in 1887 and more than 180,000 dozens (£200,000) in 1901 The production of silk articles increased sixtyfold during the latter half of the nineteenth century

The output in America is, however, not equal to the consumption, the proportion between them being 67 3 per cent for silk fabrics, 85 per cent. for ribbons, and 53 per cent for velvet. In 1901 the United States imported silk wares to the value of £5,760,000, now diminished to £3,200,000—43 per cent. from France, 18 per cent. from Japan, 17 per cent. from Germany, and 16 per cent. from Switzerland. The American Government have several times, by offering prizes, attempted to initiate the cultivation of mulberries and the rearing of silkworms, but with poor success, probably because skilled agricultural labour is lacking and is not easy to form rapidly, and also because labour is expensive.

The attempts which have been made in the Argentine have been somewhat more successful but not altogether satisfactory. To the 800,000 mulberry-trees planted during the course of 20 years, 4.000,000 have been added during the past four years, and in 1907 the crop of cocoons was 250 quintals.

about two-thirds of all the silk conditioned in Europe, the separate amounts being as follow:

	Milan	Lyons
1881	36,652	53,480
1890	43,477	44,072
1900	72,335	60,418
1903	83,725	66,508
1905	94,391	70,102
1906	101,484	71,719
1908	95,293	73,728

In 1908 13,186 quintals arrived at Lyons from Europe, 7564 from the Levant, and 50,000 from the Far East; and at Milan, 67,187 quintals from Europe, 1477 from the Levant, and 36,530 from the Far East. During recent years Milan has lost ground compared with Lyons.

SEA SILK (*Byssus*) is found in tufts protruding from the shells of a mollusc (*Pinna nobilis*), 30 to 40 cm. long and 15 to 20 cm. broad, attached to the rocks of the Red Sea and the Mediterranean (Sicily, Sardinia, Elba). It has a pale golden, more or less brownish colour, and sometimes shows greenish reflection. After being washed with soap and water and dried in the shade, it is combed and spun like other textile fibres. Although sometimes regarded as an abundant product, it is in reality rare, at least in Italy, and figures rather in museums than on the market.

ARTIFICIAL SILK is the inaccurate name given to the product which has been for some time on the market in competition with natural silk. There is, indeed, no chemical relation between the two products. In place of the fibroin and sericin produced by *Bombyx mori*, the new silvery thread contains merely cellulose, as is the case with so many other vegetable products. It has, however, the lustrous appearance of natural silk and only by reason of this property does it compete with the latter.

The struggle between the natural and the artificial product has scarcely begun and it is not easy to foretell within what time and what limits the one or the other will be victorious. We are certainly on the eve of neither a serious convulsion in the agricultural industry nor the disappearance of the mulberry and silkworm, but it may be affirmed that artificial silk has established a position in the making of certain fabrics formerly obtained solely from the natural product.

But the new artificial fibre has still many defects which limit its use, *for the present*, to definite branches of the textile industry, and time is thus given to the producers of natural silk to repair the grave error, committed in the past, of spoiling their valuable product by excessive weighting, and so injuring its sale.

The first beneficial effect of the appearance of artificial silk should hence be to bring the silk industry to the sound basis on which it was built, and which would enable it to withstand any artificial competitor for many years to come.

The prime material for the preparation of artificial silk is cellulose, that remarkable substance which has so simple a composition—carbon, hydrogen, and oxygen—but so complex and highly polymerised a molecule (*see* p. 503), and already yields so many most important industrial products—from mercerised cotton to celluloid and pegamoid, from guncotton to collodion, from explosive, smokeless gelatines to alcohol, and finally to artificial silk.[1]

Artificial silks of various different types are met with on the market:[2]

[1] When cellulose is in the form of wood for fuel, 1 cu. metre costs about 6*s*., the same cubic metre of wood, when boiled with lime, soda, and sulphite gives a paper pulp worth about 32*s* and yielding paper valued at 56*s*, or more. But if this pulp is transformed into artificial silk, its value may be as high as £80 to £240, according to the articles prepared (artificial hair and silk, cellulose acetate).

[2] Artificial silk, although of recent preparation, has already an interesting history. As early as 1734 Réaumur foresaw the possibility of preparing lustrous fibres, similar to silk, from gummy or adhesive substances, and in 1885 Audemars (of Lausanne) attempted but with imperfect success to put Réaumur's idea into practice.

Expectation of success in the solution of this important problem arose only later when it was found possible to prepare slender collodion fibres for the manufacture of the carbon filaments of incandescent electric lamps. In 1885 Count Hilaire de Chardonnet of Besançon, then a student at the Paris Polytechnic, filed a patent for the manufacture of artificial silk by spinning collodion solutions, and at the Paris Exhibition of 1889 he showed his first machine working. Swan, in London, had previously obtained fibres of artificial silk, but these were without practical interest.

In 1891 de Chardonnet formed a company at Besançon with a capital of £240,000, for the manufacture of this new product on a large scale.

But for some years de Chardonnet silk could not be used as it was composed of nitrocellulose, and hence highly

(1) That obtained by the denitration of collodion cotton previously dissolved in a mixture of alcohol and ether and then reduced to very fine fibres by means of special spinning machinery (de Chardonnet, Lehner, Viviers) (*see also* Details of working methods).

(2) That prepared by passing hydrocellulose (mercerised cotton) dissolved in ammoniacal copper oxide solution, through very fine capillary glass tubes so as to obtain—after complete coagulation in a bath of sulphuric acid at 16° to 20° Bé. or one of 5 per cent. caustic soda—filaments so slender that 225,000 metres do not weigh 1 kilo (Pauly or Fremery and Urban silk).[1]

(3) That obtained by decomposing, with ammonium sulphate, cellulose thiocarbonate (sodio-cellulose xanthate), suitably matured (*i.e.* polymerised) and converted into slender fibres by being forced through a platinum plate furnished with eighteen very small orifices so as to give simultaneously eighteen filaments, 1,000,000 metres of one of these weighing less than 1 kilo (*viscose silk* of Cross, Bevan, Beadle, Stearn, and Tophar, 1892–1900).[2]

(4) The silk prepared from *cellulose acetate* by Cross and Bevan seems to be free from the defects mentioned above and to be superior to all other artificial silks in its resistance, which is equal to that of natural silk. The manufacture of this was started a few years ago by Count Donnersmark, using acetic anhydride and chloroform, but it is too costly to compete with other silks, and is dyed only in dilute alcoholic solutions (Ger. Pat. 152,432). Excellent solvents for cellulose acetate have been found in tetrachloroethane and formic acid (Ger. Pat. 237,718 of 1907).

(5) Millar and Hummel's *Vandura silk*, obtained from gelatine solution and now from casein, is not used practically.

(6) K. Hofmann (Ger. Pat. 227,198 of 1909) obtains artificial silk and also hair and films, by dissolving cellulose at 220° in a mixture of concentrated phosphoric and acetic acids, and then precipitating with water or salt or alkali solution.

The raw material for the de Chardonnet and Fremery silks is cotton waste, which should answer the same requirements as that used in making collodion and guncotton. For viscose the raw material is wood-cellulose, such as is used in paper-making. Although the chemical processes are different, the final product for all three types of silk is more or less oxidised hydrocellulose; Chardonnet-Lehner silk consists of hydrated oxy-cellulose.

dangerous to the wearer and to warehouses in which it was stored, owing to its inflammability. Attempts to render the silk harmless by the addition of various substances proved futile, and the problem was solved subsequently to 1893 by the elimination of the nitro-groups combined with the cellulose and the regeneration of the latter without alteration of its lustre. When treated in this way it burns quite like other cotton or silk fibre.

But this operation is accompanied by a new disadvantage which has not yet been completely removed. On denitration, the artificial silk loses part of its resistance, and when it is wetted the resistance and elasticity diminish further by two-thirds. But in spite of this defect the product is marketable, its production being started before the Paris Exhibition of 1900 and subsequently prosecuted on a large scale.

[1] The first patent for this process was that of Despeissis in 1890, but this was not renewed in a year's time. The process was improved and rendered practicable by Pauly, Bronnert, Fremery, and Urban, and the manufacture was undertaken by the Vereinigten-Glanzstoff Fabriken of Elberfeld. Well defatted cotton waste is lixiviated with sodium carbonate and hydroxide in an autoclave for 3 to 4 hours, rinsed, bleached with cold hypochlorite solution, well washed and centrifuged. The mass is then treated with concentrated caustic soda to mercerise it and form sodio-cellulose, which is more soluble than cellulose; or concentrated ammonia is added to a mixture of the centrifuged cotton with caustic soda and copper sulphate solutions until the whole dissolves (6 to 7 kilos of cotton per 100 litres of solution). When cellulose is to be dissolved in cupro-ammoniacal solution the latter is prepared beforehand in large tanks (in cellars) containing scrap copper and concentrated ammonia solution kept in circulation by a pump which also injects air until each litre of solution contains about 15 grms. of dissolved copper. In this liquid, stirred now and then, cellulose dissolves in 6 to 8 days, the solubility increasing as the amount of copper present increases and as the temperature is lowered (between 0° and 4°). As soon as the cellulose has dissolved and the mass become dense and stringy it must be filtered under pressure, since if this is delayed two or three days the cellulose begins to undergo depolymerisation (especially in a warm place), and the mass loses its viscosity, with the result that the silk obtained is of poor quality, irregular and weak.

Spinning follows closely on filtration. The threads from the capillary glass tubes were at one time coagulated by passing them into sulphuric acid of about 20° Bé., but there is then danger of weakening of the fibre owing to excessive hydration, which is facilitated by the rise of temperature caused by the neutralisation of the ammonia. On this account it is now preferred to produce coagulation by means of 5 per cent. caustic soda, this giving a softer and more lustrous silk from which a very weak sulphuric acid bath readily eliminates the traces of copper hydrate precipitated by the soda. According to Ger. Pat. 221,041 (1908) coagulation with alkaline sulphite or bisulphite solution appears advantageous.

[2] According to F. Todtenhaupt (1909), to obtain perfect solution and transformation into xanthate, the carbon disulphide is diluted with an indifferent liquid, *e.g.* benzene, ligroin, CCl_4, &c., the sodio-cellulose being thus the more completely and easily penetrated. Before spinning, the pulp is matured by heating at 70° to 90° or by leaving for a longer time at 15° to 18°. In making viscose silk it was for some years found difficult to hit on the exact maturation-point (polymerisation of the cellulose) and to avoid excessive adhesive properties. But this difficulty has now been overcome and about 1,500,000 kilos of viscose silk are produced annually.

It must, however, be remembered that of the single thread (*bava*) of the silkworm, 6,000,000 to 7,000,000 metres are required to weigh 1 kilo.

Of the innumerable new patents for the manufacture of artificial silk, mention may be made of the following:

Lumière Bros. of Lyons dissolve the nitrocellulose in amyl acetate so as to avoid clotting (Ger. Pat. 168,173 of 1905). It has been suggested to add resin, oil, oleic acid, &c., to the solvent to economise the latter and to give a more homogeneous solution, but such additions retard the subsequent *denitration*. Also the addition of acid leads to the formation of oxycellulose during the denitration, with diminution in the strength of the silk.

To obtain Chardonnet silk, collodion-cotton is prepared in the way described in the section on Explosives (pp. 232 *et seq.*), and after elimination of the acid by thorough washing, the cotton is pressed hydraulically or centrifuged to reduce the moisture-content to 25 to 30 per cent. In this condition it is dissolved in 5 to 10 times its weight of a mixture of 3 parts of ether and 2 of alcohol, with which it is shaken for a couple of hours in revolving iron drums; de Chardonnet first prepared solutions of collodion with dried nitrocellulose, but Lehner of Frankfort found that moist nitrocellulose also dissolves in alcohol and ether, avoiding the danger of drying and also giving a more homogeneous fibre. If a little mineral acid is added to the collodion solution, the mass becomes much more fluid and requires less pressure for spinning [according to Eng. Pat. 16,932 of 1910, acetylene tetrachloride (*see* p. 102) is an excellent solvent for nitrocellulose]. The dense collodion solution is passed under a pressure of 40 atmos. through a cotton-wool filter, then left for a couple of days for the air-bubbles to escape, and finally forced first through cotton-wool and then through capillary glass tubes having a bore of 0·2 to 0·08 mm., under a pressure of 60 to 80 atmos.

The slender threads issuing from the capillary tubes under pressure and in a closed-in machine, through which a current of air passes to carry off the alcohol and ether vapour,[1] are united in a number varying from 6 to 20, and under a water-jet are wound on glass spools in a coagulated condition, but still somewhat adhesive owing to the moisture left in the nitrocellulose. After a short time on these spools the fibre solidifies completely and can be manipulated without danger of the filaments adhering. It is then combined, twisted, and reeled in the same way as silk.

The artificial silk fibre thus obtained is as lustrous and strong as natural silk, even in the moist state. But it has a rather horny feel, is completely impermeable to water, and hence cannot be dyed in vat, while it exhibits also the serious disadvantage of ready inflammability, which came to be avoided by elimination of the nitro-groups (1893).

Ferrous chloride, formaldehyde, thiocarbonate, &c., were tried as denitrating agents, but the best results were obtained with hydrosulphides of ammonium, calcium (0·4 to 0·5 per cent. solution), and magnesium, and with dilute sodium sulphide solution acting for 3 to 4 hours in the cold. The denitration must be carried out with great care since if as little as 0·1 per cent. of nitrogen remains, irregular striations are obtained on dyeing. In practice all but 0·05 per cent. of N can be eliminated, it being impossible to push the denitration as far as the disappearance of the diphenylamine reaction without considerable attack of the fibre. The regularity of the dyeing is also largely influenced by the manner in which the white silk is first dried. Too rapid drying at a temperature above 70° and with too dry air, gives rise at many points to oxycellulose which alternates with hydrocellulose and hence gives rise to non-uniformity of tint.

After denitration, the silk contains only minimal traces of nitro-groups, but these are in sufficient amount to allow of the distinction of Chardonnet silk from other artificial and from natural silks, by means of the diphenylamine reaction. Artificial silks may also be differentiated from natural silk by microscopic examination (*see* Figs. 442, 443).

Denitrated silk is less resistant and, as with other qualities of artificial silk, the resis-

[1] Part of the alcohol and ether used in the Chardonnet process is recovered by passing the air rich in such vapours into a receiver containing oil or fatty acids, which retain the ether, while the alcohol in the solutions used for coagulating the silk fibre is recovered by distillation or rectification. Claude (1909) proposes to recover ether and alcohol from air containing 12 to 20 grms. per cu. metre by compression under 4 atmos and by passing the air through the coils of a liquid-air machine. In the first coils the water condenses, in the higher cooler zones the alcohol, and at the top of the coil (where the temperature is −90°) the whole of the ether, the vapour pressure of the latter being 0 5 mm. The purified air, which is still under a pressure of 4 atmos, is allowed to expand in a gas-engine to recover part of the energy of compression Even when the air contains only 0 5 grm. of alcohol per cu. metre, this process admits of the recovery of 75 per cent.; 20 cu. metres of air are treated per horse-power-hour (*see also* p. 703).

tance is considerably less in the moist state; under such conditions it can still compete with heavily weighted natural silks.[1]

In general a fibre of artificial silk can be distinguished from one of natural silk owing to the small resistance of the former to tension when in the moist condition.

In bleaching artificial silk, the latter is passed first into a weak sulphoricinate bath at 40° and then into a weak bath of sodium hypochlorite and acetic acid or of calcium hypochlorite (0·15 per thousand) or of permanganate (*see* Cotton). It is then dried, the loss in weight (water and denitration) being nearly 50 per cent.

When the artificial silk factories supply a *homogeneous* product, dyeing is usually accomplished without difficulty on skeins of yarn, just as with cotton and silk. The methods of dyeing are those used for cotton or, more exactly, for mercerised cotton, which is also cellulose. The dyeing can be carried out without special mordants if substantive dyestuffs (diamine, benzo, congo, &c.) are used in a bath of sodium sulphate and a little sodium carbonate at the temperature of 50° to 60°, various precautions being taken in the manipulation.

With basic dyes, a tannin or tartar emetic mordant is used, just as with cotton, the

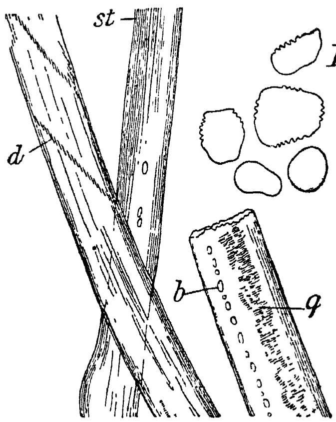


FIG 442.—(Pauly) *d*, sign of crossed fibres; *st*, striation; *b*, air-bubbles; *q*, fine transverse striations; *B*, sections of fibres

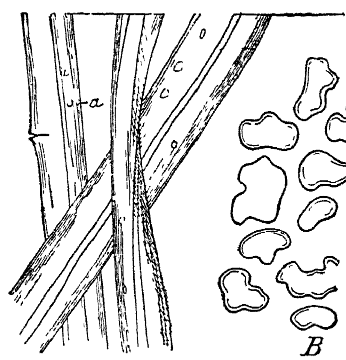


FIG. 443.—(Chardonnet) *a*, air-bubbles; *B*, sections of fibres

[1] According to Hassack the strengths are as follow:

	Elasticity	Tenacity in kilos per sq mm. Dry	Moist
Natural silks boiled and lustred	20	37 5	35
,, ,, red, slightly weighted	20	20 0	15 6
,, ,, blue-black, 100 per cent weighting	20	12 1	8 0
,, ,, black, 140 per cent. weighting	20	7 9	6·3
,, ,, ,, 500 ,, ,,	20	2 2	—
Cellulose acetate silk	17	10 2	5·8
White Chardonnet silk	} 9	14·1	1·7
Lehner (Frankfort) silk		17 1	4 3
Pauly (Elberfeld) silk	14	19 1	3·2
Viscose silk	14	21 5	—
Cotton thread	14	11 5	18·6

The *elasticity* is the elongation exhibited by 100 cm of the fibre before breaking. The *tenacity* or *resistance* of natural silk is 3 to 13 grms. for the single thread (bava). Echallier (Lyons) has recently increased the resistance of viscose in the moist state by treating it in a bath containing 15 per cent. of formaldehyde, 5 per cent of alum and 5 per cent of lactic acid

A further disadvantage of artificial silk is its high specific gravity, the same weight of yarn of the same size giving a larger quantity of fabric in the case of the natural silk than with the artificial But while, with the first artificial silks, the excess of specific gravity was 15 to 20 per cent, the difference is now reduced to 7 to 8 per cent., and further progress in this direction is not improbable Natural silk has the sp gr. 1 36 and cellulose acetate silk 1 251, while other artificial silks show values exceeding 1 5.

Marked advances have been made also in the count of the thread. Until a few years ago, only yarn of 120 denari (75,000 metres per kilo) could be made, but nowadays counts of 80 denari (112,000 metres per kilo) are regularly spun, and in some cases, with Lehner silk, 40 denari (225,000 metres per kilo) has been reached. These are still far from the fineness of natural silk (10 to 20 denari) but represent an appreciable step forward.

The machinery used in spinning artificial silk has now undergone further improvements which permit of the production at once of bundles of threads, these being subjected during their development to rapid rotation so that the completely twisted yarn is obtained in a single operation. There are also machines which give two bundles of threads twisted in opposite directions and at the same time wind the two bundles one on the other so as to produce finished organsine of two threads.

dyeing being commenced in the cold and terminated at a gentle heat in presence of 2 to 3 per cent. of acetic acid. Certain basic colours dye Chardonnet silk even without mordanting. The new sulphur colours are also used.

These different processes give all colours, from the pale and more delicate ones to black, in all shades. One merit of artificial silk is that it cannot be weighted so heavily or so easily as natural silk. Only when black can it be relatively heavily weighted.

Cellulose acetate silk is not readily dyed by aqueous solutions of colouring-matters, but as it easily fixes phenols even from dilute solution, a fine paranitraniline red can be obtained by passing the silk into a hot 0·5 per cent. β-naphthol bath and then into a 1·5 per cent. p-nitraniline hydrochloride bath containing sodium acetate.

The most valuable property of artificial silk is its great lustre, which exceeds that of natural silk and permits of its use for a large number of different articles. Beautiful new effects are obtained by using it as weft in figured textiles with warp of natural silk, a new opening being thus provided for the latter. It is also used with advantage as weft in silk ribbons. For some years it has held almost undisputed sway in the lace industry, and a single Italian manufacturer of this material consumes annually 15,000 to 20,000 kilos of artificial silk. Fringe and cord for ornamenting garments, lace, embroidery, &c., are now largely made from artificial silk. Special articles which cannot be obtained with natural silk are made from the artificial product. There is now a large consumption of *artificial hair* prepared from artificial silk by fusing together several thin fibres so as to form a single large compact filament which, unlike large fibres obtained directly by spinning, is flexible and resistant. This artificial white hair, which can be dyed various colours, is in great demand as a substitute for horsehair, which is difficult to bleach and also rather expensive owing to the increased demand for horses for military purposes. This hair is used for various ornaments but mostly for making wigs for ladies and artificial bristles.

Another interesting application of artificial silk is in the manufacture of incandescent gas-mantles according to Plaissetty's patent: such mantles are more resistant to shock, even after burning, and can be used in trains.

Largely used also is a new product obtained from viscose, namely, a kind of *ebonite*, which serves well for the manufacture of artistically worked and coloured umbrella handles, knife handles, &c., and resists the action of the acids and alkalis with which it is likely to come into contact.

Casein products,[1] which have also been suggested for these purposes, cannot compete with viscose ebonite, which exhibits marked advantages over bone and horn in the manufacture of brushes, as it can be more easily worked and more easily pierced to allow of the fixing of the bristles.

As hair-ornaments for ladies, great use is made of artificial silk in thin sheets or ribbons showing brilliant colours and sparkle. Artificial silk is also used in large quantity for making materials for tapestry, upholstery, neckties, hat-linings, &c., with which no resistance to the action of water is required. With zinc salts viscose smeared on paper or fabric shows fine silky effects and fine results are also obtained with bronze powder made into a paste with viscose and spread on different cloths.

Important new outlets would offer themselves for artificial silk if the resistance to the action of water could be improved. It seems to be a question of saturating the hydroxyl groups of hydrocellulose so as to render the latter stable towards water, and the most promising attempt yet made is that with cellulose acetate, which gives a silk highly resistant but as yet too expensive, since acetic anhydride is used in its manufacture, while the cellulose acetate must be dissolved in chloroform to be spun. In America this new product is used as an electrical insulator (its *dielectric constant* is 4 and that of viscose 7, compared with 5·6 for porcelain).

The last patents of the Badische Anilin- und Soda-Fabrik in 1904 and the more recent ones of Friedrich Bayer and Co., indicate that a speedy solution of this important problem may be hoped for.

[1] According to a Dutch patent of 1911 (No 431,052), part of the casein suited to the manufacture can be separated by precipitating the unsuitable casein (which gives brittle products) from skim-milk by means of sodium pyrophosphate solution (3 grms. of the salt per litre of milk). From the decanted liquid, the soluble part of the casein is then precipitated by means of dilute acid This precipitate is pressed, dissolved in a little dilute ammonia, filtered, reprecipitated with acid, again pressed, rendered plastic with a little ammonia and spun; the thread is rendered insoluble by means of dilute formaldehyde solution.

In Europe there are 30 large artificial silk works, with a capital of more than £2,400,000, among these being the original Chardonnet factory at Besançon, which produces 2000 kilos of silk per day, and the equally important ones at Frankfort and Tubize (Belgium), and that of the Glanzstoff Company at Elberfeld. In France there are 7 factories working profitably; in Germany, 8, Belgium, 3; England, 2; Spain, 1; Austria-Hungary, 4; America, 3; Russia, 3; Japan, 1.

The world's production of artificial silk was about 2,500,000 kilos in 1905 and more than 6,000,000 kilos in 1911, about 2,500,000 being nitrocellulose silk, an equal amount ammoniacal copper oxide silk, and nearly 1,500,000 kilos viscose silk. The output in France was about 1,700,000 kilos in 1908, the exports being 63,700 kilos in 1908, 78,500 in 1909, and 161,700 in 1910.

Italy consumes large quantities of artificial silk. The three large Italian factories (Padua, Pavia, and Turin) are working under adverse conditions owing to the excessive cost of patents and the keen foreign competition. As is shown by the following figures, the importation of artificial silk into Italy is continuously increasing:

	1905 kilos	1906 kilos	1907 kilos	1908 kilos	1909 kilos	1910 kilos	
White .	275	12,900	25,500	38,250	68,822	210,000	(£126,030)
Dyed . .	2,338	8,080	10,920	2,762	1,080	1,560	(£1,060)

The exports were:

White . .	—	—	572	18,890	82,472	83,942	(£50,365)
Dyed . .	—	—	5,238	1,187	5,299	5,422	(£3,685)

The exportation is mainly from the works at Padua, which is under contract to send its whole output to a German factory. In order to withstand competition better, the artificial silk factory at Pavia began in 1911 to use the ammoniacal copper oxide process instead of that with nitrocellulose which had been previously employed.

Artificial silk, which was sold at 28*s.* to 32*s.* per kilo in 1903 and 1904, could be bought at 20*s.* in 1905, while the price fell to 16*s.* in 1906, 13*s.* 6*d.* in 1908, and 12*s.* in 1910, the poorer qualities being sold at 6*s.* to 8*s.* per kilo.

When artificial silk can be placed on the market at 8*s.* to 10*s.* per kilo—and this would appear likely at no distant date, owing to the early lapse of the principal patents—a new era of activity for this industry will begin, as it will become possible to displace not only tussah silk but also all the heavily loaded silks of the fabrics commonly used more especially as tram silk.

The most authoritative information indicates that the cost of manufacture of Chardonnet silk should not now exceed 9*s.* 6*d.* per kilo, allowing for the recovery of most of the alcohol and ether (this seems to be effected successfully by passing the air containing them through higher alcohols such as butyl or amyl, or by washing the fresh fibre on spools with water; *see also* Note, p. 700), while that of the Glanzstoff (Elberfeld) artificial silk should ultimately fall to 6*s.* to 7*s.* per kilo, and that of viscose silk to 5*s.* to 6*s.*

These figures explain the almost fantastic profits realised by the principal factories, which have sold concessions and rapidly redeemed the cost of their plant and are now enabled to pay dividends of 50 per cent., 100 per cent., or even more.

CHEMICAL TESTS FOR RECOGNISING DIFFERENT TEXTILE FIBRES

The commonest test for distinguishing animal from vegetable fibres consists in burning a thread; the former burn slowly, giving an odour of burnt nails and forming a round granule of carbon at the point of the thread where combustion ceases, while vegetable fibres burn more rapidly, are converted into ash and give but little smell, which recalls that of burnt paper. Other reactions are as follow:

Boiling 10 per cent. caustic potash: Hemp, jute, flax, cotton, and artificial silk are insoluble and are not coloured (excepting jute, which becomes yellow); wool, silk, and artificial gelatine silk dissolve after a few minutes.

Cold conc. sulphuric acid (after 2 hours): Hemp, flax, jute, cotton, unweighted silk, and artificial silk are soluble or almost so, hemp being coloured brownish yellow, jute

brownish black, and mercerised cotton yellowish, while the rest remain colourless. Wool and weighted silk do not dissolve.

Boiling zinc chloride (60° Bé.): Flax, hemp, jute, and cotton are insoluble, jute alone being coloured a faint brown. Wool, silk, and artificial silk are soluble.

Schweitzer's reagent (see p. 503), after 2 hours in the cold, dissolves more or less completely (better if freshly prepared), hemp, flax, jute, cotton, unweighted silk (in less than an hour) and artificial silk. Wool is insoluble.

Millon's reagent (solution of mercury in an equal weight of nitric acid of sp. gr. 1·41, first cold, then heated gently, diluted with double the volume of water and decanted after standing): Cotton, flax, hemp, and Chardonnet-Lehner artificial silk are not coloured; jute is turned yellow, wool and pure silk violet-red, and weighted silk and tussah silk ochre-red.

Conc. aqueous fuchsine (just decolorised with NaOH): Wool and silk are coloured red, while cotton and flax remain uncoloured.

Silver nitrate solution: Wool is coloured violet to black, while cotton and flax are not coloured.

Iodo-zinc chloride solution (1 part iodine + 5KI + 30 fused $ZnCl_2$ + 14 water) in the cold: Flax, hemp, cotton, and artificial silk are coloured violet-brown (mercerised cotton almost black); jute, wool, and tussah silk are turned yellowish and with time become colourless; true silk is not coloured.

Lowe's reagent (shake 10 grms. copper sulphate, 100 c.c. of water, and 5 grms. of pure glycerine and add caustic potash in quantity scarcely sufficient to redissolve the precipitate formed) in the cold dissolves only natural silk and is used for the quantitative separation of natural from artificial silk.

Diphenylamine sulphate (1 grm. in 100 c.c. conc. H_2SO_4) in the cold: Hemp, flax, jute, and tussah silk are dissolved, giving more or less intense brown colorations (flax dissolves less easily and is less coloured); cotton and wool dissolve with yellow coloration; silk dissolves, giving a colourless or faintly brown solution; *artificial silk* assumes an intense, characteristic blue colour.

Molisch's reagent (obtained by dissolving 15 grms. of α-naphthol in 100 c.c. alcohol): the fibre, dyed or otherwise, is first purified by boiling with 2 per cent. sodium carbonate solution and washing thoroughly with water. One centigramme of the fibre is treated with 1 c.c. of water, 2 drops of Molisch's reagent, and 1 c.c. of conc. H_2SO_4; all the vegetable fibres, including artificial silk, dissolve with a violet-blue coloration; wool is insoluble and is coloured reddish; silk is dissolved, giving a reddish (or, if weighted, an intense red) solution; tussah silk dissolves, yielding a yellowish solution.

Iodine solution (1 grm. KI, 100 c.c. H_2O, and excess of iodine): 0·1 grm. of the white fibre, purified as above with sodium carbonate, is treated with a few drops of iodine solution, the excess being removed by means of filter-paper; hemp, flax, cotton, and artificial silk are coloured blackish brown (flax more intensely than hemp and unmercerised cotton reddish brown); wool and silk become orange-yellow and jute reddish yellow.

QUANTITATIVE ANALYSIS OF MIXTURES OF TEXTILE FIBRES

It is often of importance for trade or fiscal purposes to determine quantitatively substances extraneous to textile fibres in order to ascertain their *commercial weight*. This is determined by means of the so-called conditioning.

In *conditioning*, which is now carried out officially, the moisture is estimated by drying in an oven with automatic regulation, and thus determining very exactly the amount of dry fibre (absolute weight) remaining after silk has been heated at 120° or wool and cotton at 105° to 110°. To obtain the commercial weight the absolute weight is increased by the normal moisture which the hygroscopic fibre absorbs from the air, this being fixed at 12 per cent. for *flax* and *hemp*, 13·75 per cent. for *jute*, 8·5 per cent. for *cotton*, 18·25 per cent. for combed *wool*, 17 per cent. for spun and carded wool, and 11 per cent. for *silk* (120°); also the amount of dressing in the fibre must be deducted. It is, however, to be noted that usually wool has only 11 per cent., silk 8·5 per cent., and cotton 7·5 per cent. of moisture when in ordinary surroundings.

Dressing: 5 grms. of the fabric are well washed with water, wrung out, boiled for

15 minutes in 150 c.c. of 0·1 per cent. sodium carbonate solution, washed in water and rubbed—all the fibres being grasped—heated to boiling with 150 c.c. of 1 per cent. HCl and kept on the steam-bath for 15 minutes, again washed and rubbed, boiled for 15 minutes with distilled water, washed with cold water, pressed in a towel, washed two or three times with alcohol and two or three times with ether, dried in the air and then in an oven to constant weight.

The loss in weight, after allowing for the moisture (*see* preceding determination) represents the dressing and colouring-matter ; the latter is almost always a negligible quantity, but in the case of black may be taken at about 0 3 per cent. of the weight of the pure fibre.

Mixed Cotton and Wool Fabric. After the moisture and dressing have been determined, the cotton may be estimated and the wool deduced by difference or vice versa. The cotton is determined by boiling 3 grms. of yarn or fabric with 100 c.c. of 10 per cent. caustic potash solution, the wool quickly dissolving ; the residue is well washed with water, boiled for 15 minutes with distilled water, squeezed, washed with alcohol and with ether, and finally heated at 100° to 105° until of constant weight, representing the dry cotton. In reducing this to percentage, account is taken of the moisture and of the dressing. If, however, the wool is to be determined directly and the cotton by difference, 3 grms. of the fabric are boiled for 15 minutes with 0·1 per cent. sodium carbonate solution, rinsed in water, well wrung out in a towel and left for two hours in cold sulphuric acid of 58° Bé. ; it is then washed in a large amount of water—care being taken that the remaining wool does not become heated—boiled for 15 minutes in distilled water, squeezed, washed with alcohol and with ether, and dried at 100° to 105° until of constant weight, which represents the dry wool.

Mixed Cotton and Silk Fabric. After the moisture and dressing have been determined (*see above*), the same piece of dried fabric is immersed for a minute in a boiling solution of zinc chloride (60° Bé.) and washed first with water slightly acidified with HNO_3 and then with pure water until the wash water gives no zinc precipitate with ammonium sulphide, the remaining *cotton* being washed with alcohol and with ether and dried at 100° to 105° until of constant weight ; the silk is calculated by difference. In the case of tussah silk, the action of the zinc chloride is prolonged somewhat. In order that no loss may occur with a heavily weighted silk, the dressing is eliminated by means of sodium carbonate alone, treatment with hydrochloric acid being omitted.

Mixed Wool and Silk Fabric. The silk is dissolved in zinc chloride and the residual wool weighed, the silk being determined by difference (*see above*).

Natural and Artificial Silk Fabric. The natural silk is dissolved in Löwe's reagent (*see above*).

Cotton and Linen Fabric. As a rule the different fibres can be separated by hand, but when this is not possible the cotton (after the moisture and dressing have been determined on the same piece of fabric) is dissolved by immersing the tissue for 1 to 2 minutes in concentrated sulphuric acid ; the fibre is washed well with water—being rubbed meanwhile—then with water and ammonia, and again with water, the linen remaining being dried and weighed. The cotton is obtained by difference.

Different Artificial Silks. Those from nitrocellulose (de Chardonnet, Lehner, &c.) contain traces of nitro-derivatives and with diphenylamine and sulphuric acid give a blue reaction, which is not shown by other silks. P. Maschner (1910) distinguishes different silks by treatment with concentrated H_2SO_4 ; that from nitrocellulose colours the liquid a faint yellow only after 40 to 60 minutes ; ammoniacal copper oxide silk is coloured yellow or brownish yellow immediately, while the liquid becomes brownish yellow after 40 to 60 minutes ; viscose is at once coloured carmine-red, the liquid turning brown after 40 to 60 minutes. The fibres dissolve after about 20 minutes and then carbonise.

DYEING AND PRINTING TESTS ON TEXTILE FIBRES

Of some importance are the tests which admit of the classification of colouring-matters according to their basic, acid, neutral, or mordant character. To this end, dyeing or printing tests are made on a small scale with wool and cotton (*see also* p. 671 *et seq.*). Tests made with *colorimeters,* which compare the intensities of coloration of solutions in tubes of equal lengths or vessels of equal thickness, are of little practical value. Hence to ascertain

the dyeing power of any commercial product, the latter is compared with a standard colouring-matter by weighing out equal quantities (0·1 to 1 grm. per litre of water) of the two, and dyeing equal weights of wool, cotton, or silk fabric with definite volumes of the more or less diluted solutions. The quantity of dye used is always referred to the weight of the fabric, independently of the dilution of the bath ; this is especially the case with wool (0·1 per cent. of the dye for pale colours and 2 to 4 per cent. for dark colours). The dyeing tests are made on 1 to 2 grms. of wool or cotton yarn or tissue in glass or porcelain beakers of 150 to 250 c.c. capacity, these being heated in a bath of concentrated sodium sulphate solution or of glycerine giving a temperature of 101° to 102° in the dye-bath (*see* Fig. 444).

If the bath retains much colour after the dyeing, a second portion of the textile is dyed without adding fresh dye. If the cotton is raw it must first be boiled for an hour in a 0·5 per cent. caustic soda solution, and then thoroughly rinsed with water. If light colours are used, the cotton is also bleached in calcium hypochlorite solution (less than 1° Bé.) at 25° to 35° for an hour, washed with water, immersed in a 1 per cent. sodium bisulphite bath (*antichlor*), and well rinsed in water. Wool, if impure, is heated at 60° for 10 minutes with a solution containing 0·5 per cent. of soap and 0·1 per cent. of sodium carbonate, and then well rinsed with water. Also silk, if not already discharged, is washed with hot soap solution.

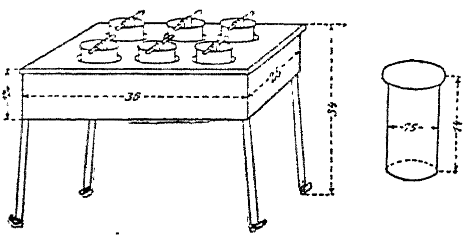


FIG. 444.

The comparative dyeing tests should be made on equal quantities of textile fibre wetted uniformly before introduction into the dyeing bath. Silk is dyed like wool, but the bath is made less acid and the temperature rather lower. Wool is dyed in an aqueous bath containing 10 to 15 per cent. of sodium sulphate and 5 per cent. of sulphuric acid (or 6 to 7 per cent. of sodium bisulphate—the German *Weinsteinpreparat*—in place of the sulphuric acid) calculated on the weight of fibre ; the bath is stirred continually with a glass rod and heated gently to boiling, being kept slowly boiling for 20 to 30 minutes ; the wool is then rinsed and dried either in the air or in a water-oven. The above procedure is followed more especially for acid dyes ; with basic dyes, one-quarter of the amount of sulphuric acid is sufficient. When wool is dyed with acid dyes, it is not merely necessary to add to the dye-bath the quantity of sulphuric acid required to liberate the acid residue of the dye so that this can be fixed on the wool, but in order that the latter may be dyed intensely and well, 20 to 30 times the theoretical amount of sulphuric acid must be added (E. Knecht, 1888). With mordant dyes, the *wool is mordanted* with 3 per cent. of potassium dichromate and 2·5 per cent. of cream of tartar (on the weight of wool) and about 100 times the weight of water, heating gradually to boiling and maintaining this for nearly an hour, the water evaporated being gradually replaced ; the wool is then rinsed and dyed in the dye-bath, which contains a little acetic acid (1 per cent. on the fibre), and is mixed continuously and brought slowly to the boil, boiling being maintained for about an hour.

Knecht and Hibbert (1903–1905) determine the concentration of the colouring-matters in the different solutions by reduction with standard titanium trichloride solution ; crystal violet, for example, fixes 2H, giving the colourless leuco-derivative.

Cotton is dyed with *substantive dyes* in more concentrated baths (50 of water to 1 of cotton) containing 30 to 50 per cent. of sodium chloride or sulphate and 1 to 2 per cent. of sodium carbonate (on the fibre) : this is heated slowly and kept boiling for 30 to 40 minutes ; in general the bath is not exhausted and can be used for a second portion of cotton. In the case of *sulphur colours*, 20 to 30 per cent. of sodium sulphide are added to the bath and in some cases 2 to 3 per cent. of glucose, and during the dyeing the cotton is kept immersed and out of contact with the air. When *basic colouring-matters* are used the cotton is previously mordanted with 2 to 4 per cent. of tannin dissolved in water, being left in contact with this solution for 6 to 7 hours (overnight) at 50° to 60° (the tannin is fixed more slowly in the cold) ; the cotton is then wrung, immersed for 10 minutes in a bath containing 2 per cent. of tartar emetic (antimony potassium tartrate) at 40°, rinsed with water and dyed in the tepid (30° to 40°) dye-bath for 20 to 30 minutes.

Dyeing on a large scale is carried on under the same conditions, but the calculations are made on a longer time, and great precautions are taken in the moving of the fibre and in raising the temperature, so as to obtain uniformity. For dark colours, the tannin is fixed with ferric nitrate instead of with tartar emetic. Industrial dyeing apparatus is shown more in detail later (p. 717).

PRINTING TESTS. The object of printing is to colour the fabric or yarn in a definite pattern or with different colours, part of the fibre being possibly left unaltered. In the first rudimentary printing processes, the fabric was printed with resin or a kind of cement, the uncovered parts being dyed as usual and the preserving substance subsequently removed. It is now usually regarded as preferable to stamp, *i.e.* to print, on the fabric or yarn the colour mixed with *thickening* (gum, dextrin, gum tragacanth, &c.) by means of metal rolls on which the desired pattern is engraved. The engraved roll is coated with the pasty colour by rotating against a rubber or cloth roller (*furnisher*), one-half of which dips in a vessel containing the thickened colour ; a knife (*doctor*) is arranged so as to scrape the excess of colour from the metal roll, and the yarn or fabric then passes over the latter under pressure. In order to fix the colour and prevent it from spreading, the fibre is subjected for 30 to 60 minutes to the action of steam at about 105° (*see* p. 731). By this means the colour is fixed without immersing the printed fibre. The latter is subsequently washed with an abundance of cold water (or with tepid soap and water), which removes all excess of colour and thickening agent. In other cases similar effects are obtained by dyeing uniformly in the ordinary way and then printing on the dyed fabric reagents which decolorise (corrode) the dye at the points of contact. Sometimes other colours are introduced with the corroding agent, so that the white parts are dyed a lighter or darker shade or a different colour from the foundation.

A kilo of thickened colour for printing wool black—the wool having been previously subjected to slight chlorination to make it take up the colouring-matter better (by immersion in a cold calcium hypochlorite bath at 0·5° Bé. and then in very dilute HCl, washing, and drying)—may be obtained as follows: 750 c.c. of water, 100 grms. of gum, and 100 grms. of *British gum* (dextrin) are heated in a jacketed vessel by means of indirect steam and kept well mixed, 60 grms. of anthracite black E G and 10 grms. of milling yellow O (and, in some cases, 8 grms. of anthracene acid brown R) being added. When the paste is boiled uniform, it is allowed to cool, and before it is used a solution containing 80 c.c. of water, 120 c.c. of acetic acid (6° Bé.), and 40 grms. of sodium chlorate is well mixed in.

For printing cotton textiles, colours are used which form insoluble lakes with tannin or metallic oxides ; such are basic and mordant colouring-matters (alizarin, &c.). The former are dissolved in acetic acid and tannin (or a solution of 50 parts of tannin, 50 of water, and 5 of tartaric acid) and the latter (alizarin, &c.) in chromium (or iron, aluminium, &c.) acetate, dextrin, gum, &c., being added in either case. Fabrics treated with tannin, after being steamed at the ordinary pressure and before being washed, are passed into a bath containing 5 to 10 grms. of tartar emetic per litre at 60°.

FASTNESS TESTS. The fastness of a colour is only relative and must be considered with reference to the purposes for which the dyed fibre is required ; for example, it would be superfluous to require fastness against light in dyed fibres or fabrics to be used for stockings, linings, &c. The dyed specimen is mixed with similar undyed fibre and subjected to the following tests, as required. Mordanted colours answer all these tests fairly well, but in other cases more or less of the colour is given up.

Fastness against Water. The sample is immersed in 50 times its weight of cold water for 12 hours or for 1 hour in water at 60° to 70° (and is left to cool in the bath) and is then dried in the oven. Note is taken of the colour assumed by the water and by the white fibre, especially where the latter comes into contract with the dyed fibre.

Fastness against Soap, Alkali, and Washing. The skein of white and dyed fibre is immersed in 50 times its weight of an aqueous solution containing 10 grms. of Marseilles soap and 10 grms. of soda per litre. The bath is heated at 60° for 30 minutes and allowed to cool, the skein being then removed, well rinsed, and dried. The changes in colour of the bath and the white and dyed fibres are observed.

Fastness against Milling. This test is carried out with a soap and soda solution, of double the above concentration, at 40°, the skein being continually rubbed between the hands for 30 minutes, and then well washed and dried in the oven. Colours fast to milling

should not soil the white portion of the skein and should give up only a minimal amount of colour to the bath.

Fastness against Bleach. If the colour is on wool or silk it is immersed in a 2 per cent. sodium bisulphite bath acidified at the moment of using with a few drops of hydrochloric acid, and, after 30 minutes, washed and dried. When the colour is on cotton, the test is made with a calcium hypochlorite bath at 0·5° Bé. for half an hour.

Fastness against Scouring. Indigo, Turkey-red, and all basic dyes on cotton mordanted with tannin, even when dry, give up a little colour to a white handkerchief with which they are scoured. Other dyes should not soil the white.

Fastness against Acid. The test is carried out for an hour with 1 per cent. sulphuric acid at 60° to 70°.

Fastness against Perspiration. In some cases this test is made with a 1 per cent. acetic acid solution for 30 minutes at 60°, the skein being dried at 60° under slight pressure, without rinsing and after thorough rubbing. In others, an alkaline test is made—as in testing fastness against washing—but the unrinsed skein is subsequently scrubbed and dried at 60° under slight pressure.

Fastness against Ironing. The dyed tissue or yarn is ironed with a very hot iron (130° to 140°), note being taken whether, after cooling and exposure to the air for 15 minutes, the fabric resumes its original colour. Many colours are changed by ironing hot, but return to their initial state in the cold.

Fastness against Steaming. The yarn is placed in a glass tube, through which steam at 110° is passed for two or three minutes.

Fastness against Light. One half of a skein of yarn or of a strip of fabric is tightly enclosed between two pieces of card, while the other half is left free ; the whole is then hung in the open air exposed to the sun and weather. For pale colours, an exposure of at least two days, and for dark colours, one of at least four days, is necessary in summer, while in winter or in cloudy or rainy weather (the skein must be sheltered from rain), at least double or even treble these exposures are necessary. The covered and uncovered portions are subsequently compared.

Fastness of the Dressing against Rain. A few drops of water are sprinkled on the fabric, especially finer woollen ones, and after exposure to the air it is noted whether the drops have left faint spots. In some cases the fabric is scratched with the thumb-nail ; a paler streak should not result. This test is not applied to cotton fabrics strongly dressed, since the nail will sometimes detach the dressing itself.

THEORY OF DYEING. The phenomenon of dyeing was at one time thought to be due to the porosity and capillarity of fibres which were thus enabled to absorb, and become impregnated with, dyes. The possibility of chemical combination between the dye and the fibre was regarded as excluded, it being asserted that in such case the fibre would undergo marked change. The different colouring powers of substances were explained as due to different molecular magnitudes. Even at the beginning of last century, in Chreveul's time, these ideas prevailed, and only in the case of mordant dyeing was any chemical fixation of the dyestuff assumed. Later on, Bergman, J. Persoz, &c., arrived at a purely chemical conception of the phenomenon of dyeing. But when in 1885 substantive cotton dyestuffs of almost neutral character made their appearance, the chemical theory, which was based mainly on the basic or acidic nature of the dyestuffs, was in some degree shaken. Many then accepted a new theory in harmony with the osmotic phenomena of solutions, the more readily because no definite and constant relation between the amount of fibre and that of dyestuff combined had been established. The chemical theory was, and is still, however, upheld by many authorities on the subject, more particularly by Noelting, by Knecht, and by Vignon, who have pointed out that alloys form well characterised compounds which exhibit no definite chemical relations between the components and may be regarded as true solid solutions of one substance in excess of the other. Further, they were able to show that silk and wool, in combining with colouring-matters, set free the acid united with the base of the dyestuff, this acid being found in the dye-bath. Also, with certain acid dyestuffs (*e.g.* naphthol yellow), Knecht and Appleyard found a constant relation between fibre and dyestuff.

Jacquemin asserts that if there were no question of chemical combination, the dry dyed tissue should have the colour of the dry colouring-matter, whereas it has the same

colour as the dissolved colouring-matter. Nietzki finds that with certain highly basic colours (*e.g.* methyl green), wool cannot of itself displace the mineral acid of the colouring base, the addition of ammonia being necessary; while, with the same colouring-matters the more markedly acidic silk is dyed without any addition.

An interesting fact, which supports the chemical theory, is that the base of rosaniline is colourless and becomes red (fuchsine) only when converted into a salt with HCl; a similar change is produced if wool is immersed in a colourless rosaniline (base) bath, the wool being dyed red owing to the formation of a salt. If the dyeing is effected directly by rosaniline hydrochloride, the bath ultimately contains the hydrochloric acid which is displaced by the acid of the wool fibre (Jacquemin and Knecht, 1888).

Moreover Richard (1888), Vignon (1890), and Nietzki (1890) showed that silk and also wool are active both towards acids and towards bases, so that in chemical characters they are comparable with the amino-acids. The fibre may even be replaced by albumin, which is dyed by the same dyestuffs as wool, &c.

According to W. Suida (1907) the dyeing of wool is accompanied by liberation of the base of the dyestuff which combines (or forms salts) with the textile fibre, the latter functioning as a polybasic acid in virtue of its guanidyl and imidazole groups. Also Vignon showed that when wool and silk are dyed with basic or acid colouring-matters heat is developed, so that the dyeing may be regarded as a true, exothermic chemical reaction. According to Vignon cotton is not dyed directly by basic or acid dyestuffs (which are usually salts) since it has not the reactive force to decompose them; but if it is previously oxidised or animated, it fixes these dyestuffs partially with development of heat. Further, the difference in fastness against light of the same colouring-matter (*e.g.* methylene blue) fixed on cotton (with tannin) and on wool or silk would appear to favour the chemical hypothesis of the phenomenon of dyeing.

In 1889 O. N. Witt advanced a new theory, which explains also the dyeing of cotton with substantive and mordant dyes. According to Witt, dyeing consists merely of a solution of the colouring-matter in the fibre, analogous to that of solution of coloured metallic oxides in glass. So that the colouring-matter passes from a liquid solvent (dye-bath) to a solid one—the fibre itself—just as occurs with alloys or in the extraction with ether of a substance dissolved in another solvent in which it is less soluble than in ether—assuming that the two solvents are mutually insoluble.

Dyeing on mordants is similarly explained as due to the solvent properties of the fibres for the metallic salts, these then fixing the colouring-matter from the dye-bath. The dyeing of cotton with substantive dyestuffs is regarded as the result of the marked solvent power of cotton (cellulose) for these dyes. In support of his theory, Witt cites the fact that silk dyed with fuchsine gives up its colour to alcohol, which is a better solvent for fuchsine than is silk, while if the alcohol is then diluted with water, the colour is again fixed by the silk.

To this observation Knecht (1902) made the reply that, with substantive colouring-matters, lanuginic and sericinic acids form insoluble lakes, *i.e.* true compounds, while with fuchsine they form lakes soluble in alcohol; it is therefore to be supposed that the fuchsine extracted by Witt with alcohol is in reality the soluble lake formed by the fuchsine with the components of the fibre. Rosenstiehl (1894), Reisse (1896), and Gillet (1898), after various quantitative dyeing tests, decided in favour of the chemical hypothesis.

In 1894–1895 Georgievics advanced a number of arguments in favour of a purely mechanical theory of dyeing (his predecessors of a century earlier being Hellot and Le Pileur d'Apligny, and those of more recent times Walter Crum, Spohn, and Hwass). Comparing the latter with occlusion of gases by solids or with the mechanical fixation of dyes on sand or on powdered charcoal, &c., he maintained that colouring-matters fixed on fibres have the same properties as those not so fixed, and that there can hence be no question of a chemical reaction (*but see above*, Knecht's experiment), since some dyestuffs fixed on fibres can be separated by mere sublimation, while in other cases (with methylene blue and indigo carmine) the coefficient of distribution of the colouring-matter in the fibre and in the solution is constant. According to Krafft (1899), dyeing generally consists in a deposition, on or in the fibre, of adhesive and resistant colouring salts in the colloidal state.

Biltz (1905) has succeeded in producing true dyeing phenomena by replacing the textile fibre (cotton) by aluminium hydroxide or other hydroxides which behave as *hydrogels*

(*see* vol. i, p. 102) towards the colouring-matter, which is regarded as a colloid (benzopurpurin and sulphur dyes). Freundlich and Losev (1907) have shown that carbon not only fixes colouring-matters but decomposes basic colouring-matters, fixing the coloured base in the colloidal state and leaving the acid in solution, in the same way as happens with wool or silk. Knecht has recently (1909) found that the amount of colouring-matter fixed by charcoal is related to the quantity of nitrogenous matter remaining in the charcoal even after ignition, so that here a true chemical reaction occurs; this investigator has also shown that colouring-matters cannot be regarded as colloids, since they are electrolytes and diffuse through membranes.

In 1909 Dreaper and Davis demonstrated that basic colouring-matters are fixed in constant quantity on calcined sand, and in increased quantity if the dye solution contains sodium chloride. Rosenstiehl assumes that the phenomenon of dyeing is explainable by the cohesive force between the colouring-matter and the textile fibre, this force varying with the liquid or gaseous medium in which the dyeing takes place and depending on or being produced by the osmotic pressure of this medium.

According to Müller and Slassarski (1909) dyeing may be regarded as a phenomenon of *adsorption* of the colouring-matter by the colloid, *i.e.* the textile fibre. There is hence not chemical combination, but fixation under definite conditions (of moisture and temperature).

Mercerised cotton fixes colouring-matter on account of its more marked colloidal character. The process of fixation or adsorption may also be reversible and all the phenomena of direct dyeing depend on the relative coefficient of adsorption of the colloid (fibre) for the colouring-matter. Freundlich and Losev and Pelet-Jolivet attribute dyeing to *adsorption* because the fixation of the colouring-matter from solution by any textile fibre obeys the formula, $\frac{x}{m} = K \cdot C \frac{1}{n}$ (where $\frac{x}{m}$ denotes the ratio between the quantity of colour absorbed and the weight of the textile fibre, K and $\frac{1}{n}$ are constants, and C indicates the final concentration of the colouring-matter), which also regulates the adsorption of gases by solid substances and that of various dissolved substances by animal charcoal. It cannot, however, be denied that certain limited chemical processes also correspond with this formula, and that many phenomena accompanying dyeing are most simply explained chemically.

Indeed, W. J. Müller and Slassarski (1910), by means of experiments on the dyeing of artificial silk, show that the absorbed colour varies in quantity with the chemical properties of the cellulose (raw, oxycellulose, hydrocellulose).

Every hypothesis is supported by some experimental fact, and it would seem that, according to the nature of the fibre, of the colouring-matter, and of the dyeing process, the phenomenon is explainable either on purely physical or on purely chemical grounds, but more generally on both.

O. Weber (1891, 1899) and Gnehm (1898) explain the various phenomena of dyeing in the following way: (1) Dyeing on mordanted cotton is due to the formation of lakes between the colouring-matter and the mordant precipitated mechanically on the cotton. (2) Azo- colouring-matters formed directly on the fibre (*see* p. 658) or pigments held by it, ultramarine, cinnabar, ochre, Guinea green, &c.) are merely precipitates deposited mechanically in the pores of the fibre. (3) The direct dyeing of cotton with substantive dyes consists in solution of the colouring salt in the cell juice, and the marked fastness against washing of these colours on cotton is due to their slow diffusion with the juice (Müller-Jacobs and Weber). (4) Dyeing of tannin-mordanted cotton with basic or indigo colours is a true mechanical occlusion. (5) Direct dyeing of wool and silk and other animal fibres with basic or acid colouring-matters is due partly to mechanical absorption, and partly to chemical combination, of the colouring-matter by the fibre. (6) The dyeing of *mordanted* animal fibres is explained by the formation of insoluble lakes, partly by the mordant fixed chemically by the fibre, and partly by that fixed mechanically within the fibre, but is never caused by combination of the unchanged fibre with the colouring-matter.

As regards the *mordanting* of wool, it has been shown that when this is boiled with metallic salts, it fixes not only the basic part but also the acid part of the salt (only of unstable salts, *e.g.* sulphate of Al, Cr, Cu, or Fe, and not sodium sulphate or chloride); the latter part is eliminated to some extent by water, but the basic part is fixed more stably.

MACHINERY USED IN DYEING AND FINISHING TEXTILE FIBRES

The limits of this treatise do not allow of the inclusion of a complete description of all the machinery used in works where textile fibres are dyed and finished. We shall hence confine ourselves to illustrating some of the principal washing, dyeing, and dressing machines.

WASHING AND PREPARATION. At the dye-house, textile fibres arrive either raw (cotton and wool in flock) or combed (wool in skeins or *tops*) or spun in skeins or on bobbins (wool, cotton, silk), or more commonly woven in pieces 30 to 100 metres long and 60 to 140 cm. wide (woollen, cotton, silk, or mixed fabrics).

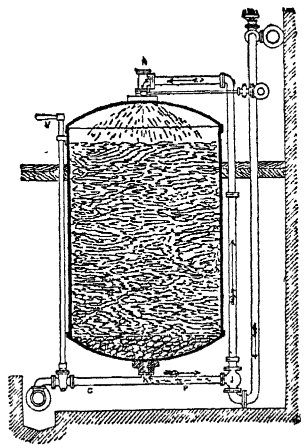


FIG. 445.

Wool is sometimes supplied free from its natural fat (*see* p. 681) but, whether as fabric or as yarn, contains the fat or dressing used in weaving or spinning.

Cotton is still in the raw state, and, in order that the colouring-matter may be fixed well, it is subjected to energetic boiling under slight pressure with water and with soda. With either flock or skein cotton, this treatment is carried out in large, closed, iron or copper boilers (Fig. 445), provided with pumps or steam-injectors for circulating the liquid, the textile material not being moved as it might be damaged. As a rule the boiler is either evacuated or freed from air by a current of steam, since air damages the fibre owing to formation of oxy-cellulose, and also gives dark lye; along with the caustic soda, vigorously frothing soap (from castor oil, for example) is introduced.

The washing of cotton goods to rid them of the starch with which the weft was charged for weaving purposes was at one time carried out by heating them with milk of lime, but better results are obtained by heating with dilute caustic soda solution in an autoclave under steam-pressure. Nowadays the goods are often passed through a lukewarm bath of *diamalt* or *diastofor* (malt extracts rich in diastase) and left in heaps overnight, the starch being thus transformed into soluble dextrin and maltose. The latter products are removed by thorough rinsing in water: the material passes between the two rollers *A* and *B* (Fig. 446) into the water, round the roller *C*, up between *A* and *B*, down again and so on until it reaches the middle, where it is removed, together with a similar piece introduced at the other end of the machine; the pieces of material are tied end to end and passed through this washer in a continuous length; an abundant supply of water enters the vessel at *D* and is drawn off through another pipe.

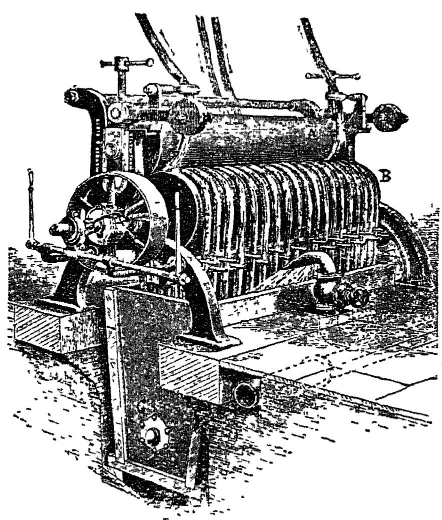


FIG. 446.

When washed the goods are *soured* with a solution of sulphuric acid (0·5° Bé.), either cold or tepid (with the latter the action is very rapid, even with more dilute acid); the pieces may be tied together in cords and passed through this solution (*see* Fig. 446). Bleaching is then effected in a clear chloride of lime bath (0·5 to 0·75° Bé): this occupies some hours in the cold, or, if the liquid is lukewarm, the material may be passed continuously through it as before. Then follows rinsing and treatment with antichlor (sodium bisulphite).

Skeins of cotton yarn may also be *bleached* with chloride of lime in an apparatus with

automatic circulation of the liquid, as is shown in Fig. 445, while the rinsing may be effected in rotating machines (Fig. 447), where each skein rotates on a reel and all the reels rotate horizontally in a circulation vessel, a water-spray being used meanwhile.

According to Pick and Erban cotton may be bleached in the cold, without preliminary boiling with alkali, by means of sodium hypochlorite solution mixed with sulphoricinate; in this way, the resistance of the fibre is retained better, while time is saved (Ger. Pat. 176,609 of 1906). Cotton or cotton and wool fabrics may be bleached by passing them repeatedly into a sodium permanganate bath (0·6 to 0·7 per cent. of the permanganate on the weight of fibre) until the bath is almost decolorised and the fibre turned brown, then into a sodium sulphite or sodium nitrite bath (0·6 to 0·7 per cent. on the fibre) and finally into sulphuric acid (4 per cent. on the fibre).

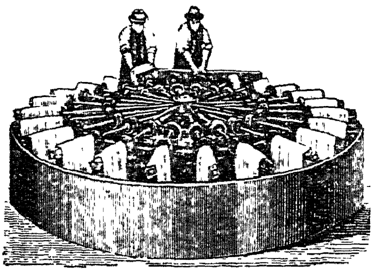


FIG. 447.

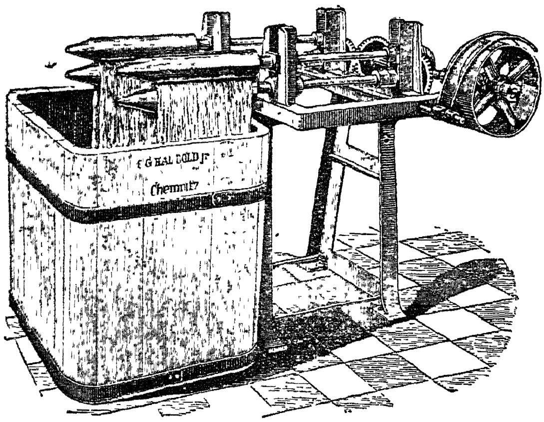


FIG 448.

The **Washing** of skeins of *wool* yarn in a tepid bath (50° to 60°) is carried out by passing the skein for a minute between two rolls (Fig. 448), then twisting the skein and again squeezing it. Subsequent thorough washing with water—in the vessel shown in Fig. 447, for example—renders the skein of wool ready for dyeing. In all these operations and in those which follow, woollen yarns are treated with greater care than cotton ones, it being necessary to manipulate, press, and rub them as little as possible and only very slowly, in order to avoid felting.

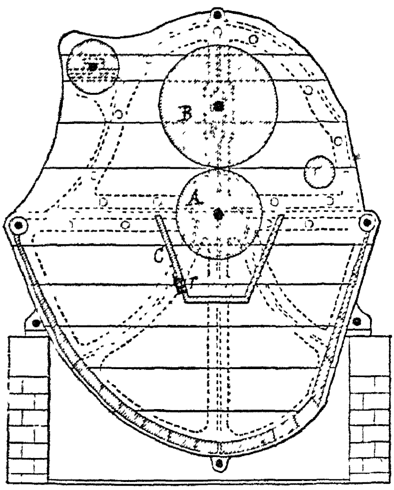


FIG. 449.

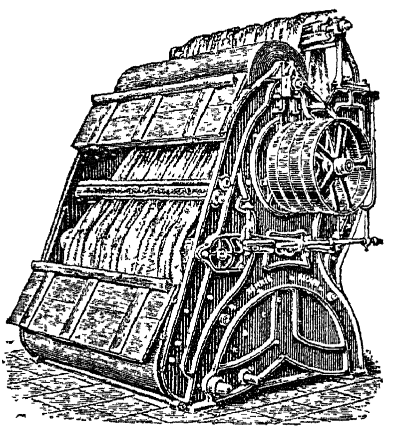


FIG. 450.

Bleaching of washed woollen yarns or fabrics (wrung out uniformly by means of centrifuges: *see* p. 468) by *sulphuring* is effected by stretching them out on rods in tightly closed chambers in which sulphur has been previously burnt in a cup situate in an angle heated by a furnace outside. Here the wool is left overnight, and in the morning the windows

are opened and the wool dried and deodorised in the air. The amount of sulphur burnt is 2 to 3 per cent. on the weight of the wool, or less if the chamber is a small one and deficiency of air is maintained in order to avoid sublimation of the sulphur and its deposition as a yellow powder in the wool.

Bleaching with Hydrogen Peroxide is carried out in the cold or at a gentle heat, and for woollen yarn, paraffined wooden vessels, or, better, cement troughs, are used. Woollen or silk fabrics are wound into a vessel similar to that used for dyeing (*see later*), or, better, on a jigger (*see later*). The bath is prepared by diluting commercial 10 to 12 vol. H_2O_2 with 8 to 10 times its volume of water, and rendering it slightly alkaline with ammonia (*see* vol. i, p. 235). After use the bath is preserved by acidification with sulphuric acid. More economical bleaching is obtained with sodium peroxide, which, however, must be used with great caution (*see* vol. i, p. 440); better results are obtained with sodium perborate (*see* vol. i, p. 480) in a bath containing, say, 200 litres of water, 600 grms. of sulphuric acid of 66° Bé., and 1·8 kilo of sodium silicate at 40° Bé.

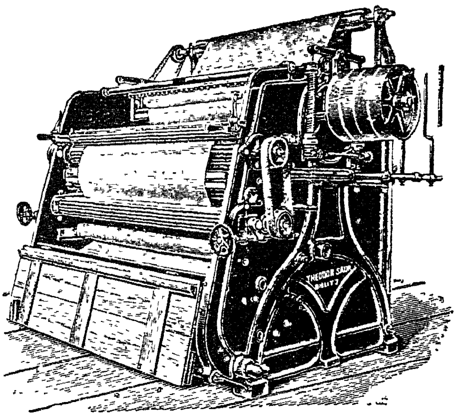


FIG. 451.

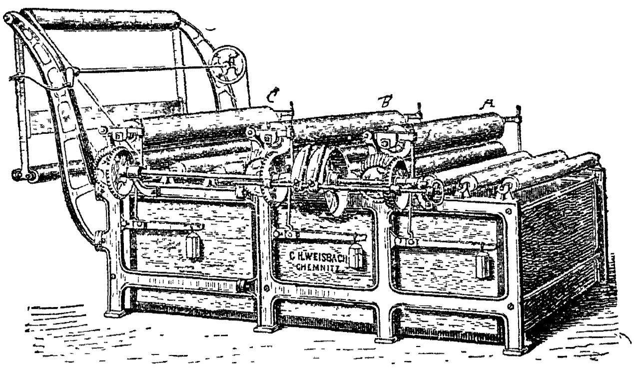


FIG. 452.

Washing of Woollen Fabrics is carried out in various ways. A number of the pieces, the two ends of each being tied together, are wound round in a trough fitted with a pair of pressure rollers, *A* and *B* (Figs. 449, 450), and containing hot soap and soda solution. Beneath the rolls is a wooden channel, *C*, to collect the expressed liquid, which for some

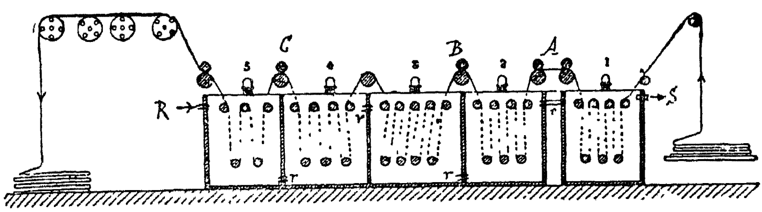


FIG. 453.

time is allowed to run back through *r*, but when dirty is run off outside. Thorough rinsing with water is carried out in the same vessel. It must be noted that almost all washing and dyeing machinery is fitted with arrangements for obtaining different velocities of the moving parts, with pipes for water and steam, &c.

Very heavy woollen fabrics are more easily washed at their full width in vessels (Fig. 451) similar to the preceding. But the lighter ones are most conveniently dealt with by joining

the pieces end to end so as to form a single piece, which is treated in the machine shown in Fig. 452, and, in diagrammatic section, in Fig. 453. This is furnished with three pairs of rolls, A, B, and C, which press the pieces in their passage from one vessel to the next, while a slow current of water enters at R and takes a zigzag course through the succeeding vessels; a little soap and soda solution is gradually added in vessels 1, 2, and 3, which are heated by steam-pipes, while the dirty water is discharged continuously from S.

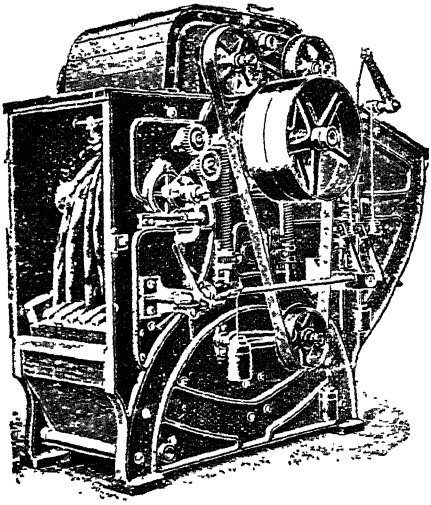


FIG. 454.

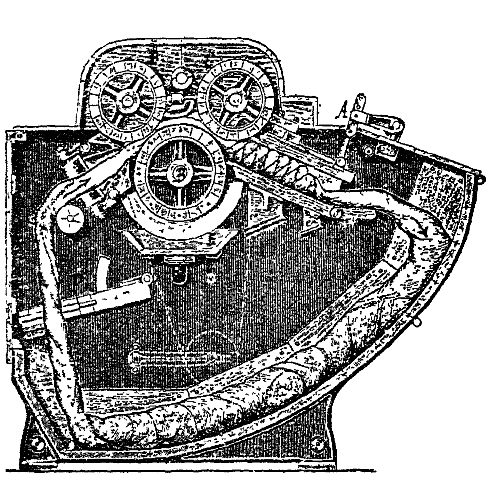


FIG. 455.

For making certain articles, woollens must be subjected to **Milling**, which transforms them into more or less close cloth.

When the pieces are rolled up, moistened with soap solution, and then continually compressed and rubbed together, the wool is felted and cloth formed in the course of a few hours. The milling machine in which this is effected is shown in Figs. 454 and 455. The material is caught between the three wooden rollers A, B, and C, which compress them and force them into the wooden channel R S, where the pressure of the plate R may be increased by the spring A; the expressed liquid collects in the channel E and is at first returned but later discharged. If any knots were formed they would stick at P and raise a spring, T, thus stopping the driving-belt. With certain heavy fabrics already soaked with oleine, milling is carried out with addition of a little soda solution, which saponifies the oleic acid. In some cases dilute sulphuric acid is used, but better results are apparently obtained with 1 per cent. lactic acid solution, the wool then retaining greater lustre and elasticity (G. Ita, Ger. Pat. 236,153 of 1910).

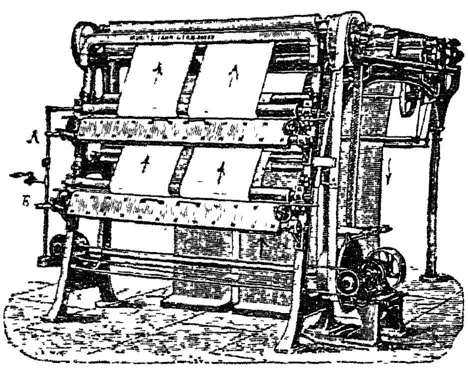


FIG. 456.

Some fabrics which are required to take bright designs and a very smooth and shiny surface (*satin*, &c.) are freed from the down always accompanying textile fibres—especially after washing, &c.—by passing them, quite taut, quickly over a row of gas-jets (or over a sheet of heated copper or a strip of metal heated electrically), which burn the hair on the face and sometimes on the reverse of the fabric too (*see* Fig. 456, where the gas-jets run horizontally from A and B).

The removal of cotton fibres or bits of vegetable matter (which would become more noticeable after dyeing) from woollens may be effected by hand, but is more commonly attained by **Carbonisation.** In this the fabric is impregnated uniformly with sulphuric

acid of about 4° Bé. (or aluminium chloride solution), centrifuged and heated at 125° to 135° —being passed at width either over a series of tinned sheet-iron or copper rollers (similar

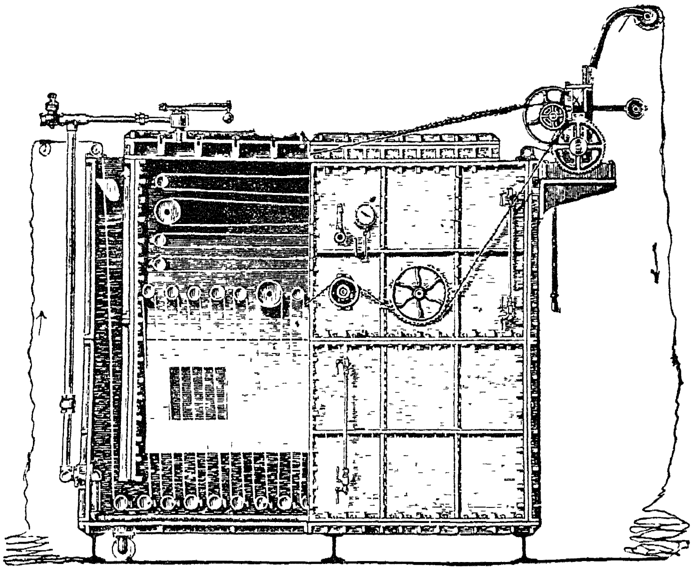


FIG 457.

to those used for drying woven goods after dyeing) through which steam at 2 to 3 atmos. is passed (*see* Fig. 481, p. 724) or else slowly through a large oven heated with hot air or with branched pipes fed with steam under pressure (*see* Fig. 457). In this way all the

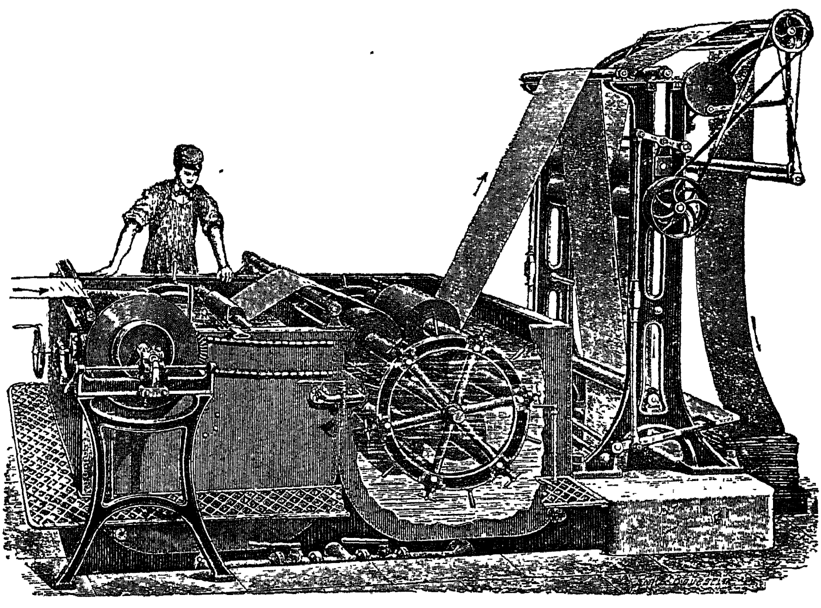


FIG. 458.

vegetable fibres are incinerated or carbonised and are eliminated in the subsequent souring, which occupies an hour and is effected by means of a large quantity of water in the washing vessels already described (Figs. 449, 450).

As has been mentioned, woollen fabrics exhibit a tendency to felt and shrink, and these actions may become very pronounced during dyeing, when the material is kept moving

in boiling baths for two or three hours. In order to avoid these changes, which likewise often spoil the design, the fabric is subjected to **Fixing**, which consists in heating it in a *stretched* condition in vigorously boiling water, *i.e.* at a temperature rather higher than any it will experience in subsequent operations ; scalding of the fibres in this way causes

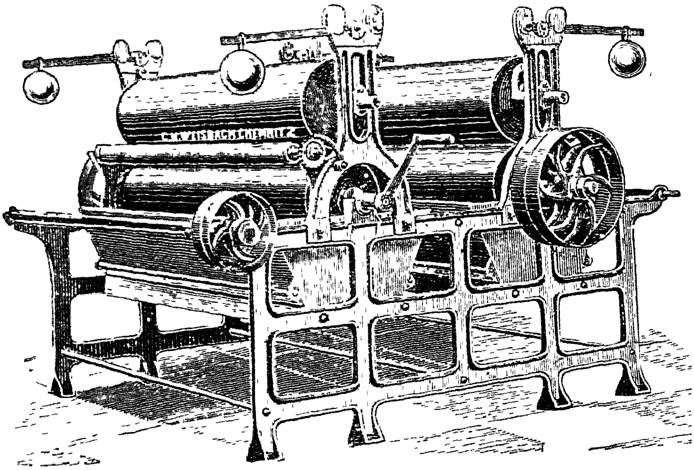


FIG. 459

partial loss of their elasticity and power of contraction, and the fabric shrinks less during dyeing. Light fabrics are fixed in the so-called revolver machine (Fig. 458), in which the material is wound in compact rolls on reels dipping into a vessel of water kept briskly boiling ; each reel may have six rolls and one reel is arranged in each of two adjacent vessels. The axis of each reel revolves during the winding, and when the first reel has

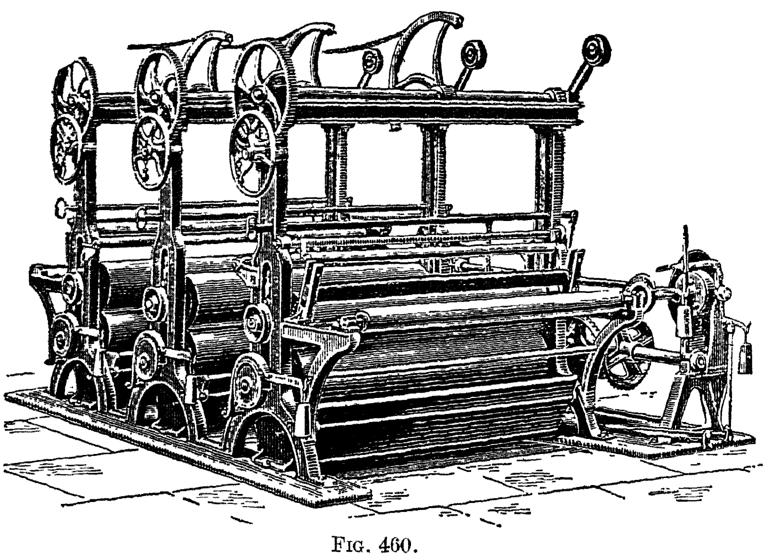


FIG. 460.

received the first six rolls, the first roll begins to unwind to form another on the second reel, so that the part of the fabric which was peripheral on the first roll becomes central in the roll of the second reel. This procedure prevents any subsequent irregularity of colouring owing to the more ready and more intense fixation of the dye on the parts subjected to the most prolonged action of the boiling water. Each roll may contain from 100 to 300 metres of fabric, which is fixed in about an hour.

Certain heavy woollens with a satin surface (and also mixed wool and cotton goods—*unions*—or cotton goods with a satin foundation) are fixed, and at the same time furnished

with a lustre which persists even after dyeing, by so-called *crabbing*. The machine in which this is carried out consists essentially of two or three pairs of superposed heavy rolls of solid iron (Figs. 459, 460). One-half of the lower roll of each pair dips into a long narrow vessel of water kept boiling by direct steam. The stretched, smooth cloth is wound in compact rolls on the lower roll, and is then allowed to revolve for 30 to 40 minutes in the boiling water, being pressed by the upper roll, which revolves freely and can be weighted by means of levers. The fabric then passes to the lower roller of the adjacent vessel and so on.

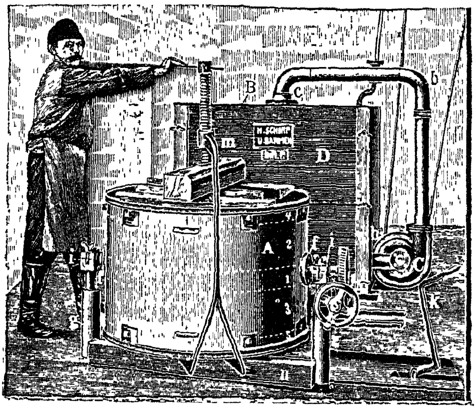


FIG 461.

DYEING. Cotton and wool in flock were at one time dyed by immersing them—in cloth or net—in open wooden vessels containing the hot dye-bath. Use was afterwards made of mechanical apparatus similar to that shown in Fig. 445, where the material remains stationary on a false bottom, below which the liquid is drawn off and pumped to the top.

It was, however, often found that the liquid did not pass uniformly through the whole of the fibre but went more easily through that which was least compressed and which contained channels, thus producing irregular dyeing. Almost universal use is now made of mechanical apparatus similar to the above, but with the fibre highly compressed (*see* Fig. 461). In this case the pump, which must be more powerful, causes complete penetration of the liquid, and much better results are obtained. Skeins of yarn can also be dyed in this apparatus when they are well compressed. After the discharge of the dye-bath (kept, if required, for a subsequent operation), the dyed fibre may be washed in the same vessel.

To dye combed wool (*tops*) wound on to bobbins by suitable machines (Fig. 462), very general use is made of Obermaier mechanical apparatus of the revolver type, in which the bobbins are arranged in as many horizontal, cylindrical cases fitting into a vertical cylinder closed at the top and communicating below with the pipe of a pump, which it fits exactly (Fig. 463); the mode of action is shown clearly by the figure. A more simple apparatus which carries larger charges and is largely used also for yarn on bobbins with crossed thread, is that of Halle shown in Fig. 464, where may be seen the false bottom supporting the bobbins, the pump for circulating the dye solution and the perforated cover pressed down by vertical screws. In these mechanical apparatus it is always possible to reverse the sense in which the liquid circulates, homogeneous dyeing being thus more easily obtained.

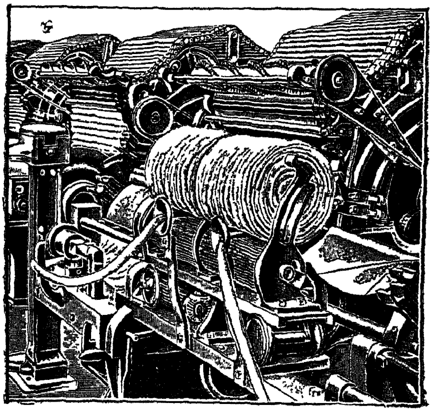


FIG. 462.

With skeins of spun fibre, various methods of dyeing are in use: in the old method, still largely used, the skeins are threaded on smooth round sticks so that one-half of the skein is immersed in the dye-bath, the skeins being turned or inverted on the stick from time to time by hand (*see* Fig. 465). The form of the wooden vessel is now simpler, as is seen from Figs. 466 and 467, which show the perforated false bottom below which are the direct or indirect steam-pipes for heating the bath, and the perforated wall, *P*, outside of which the colour is gradually added so that it may not come into immediate contact with the neighbouring skeins.

A mechanical apparatus for dyeing skeins is shown in Fig. 468. The skeins are threaded on rods which are rotated by toothed wheels, while the whole frame can be raised from or lowered into the bath by a toothed rack. Still better is the Klauder-Weldon revolving apparatus shown in Figs. 469 and 470: on a large bronze wheel, one-half of which dips

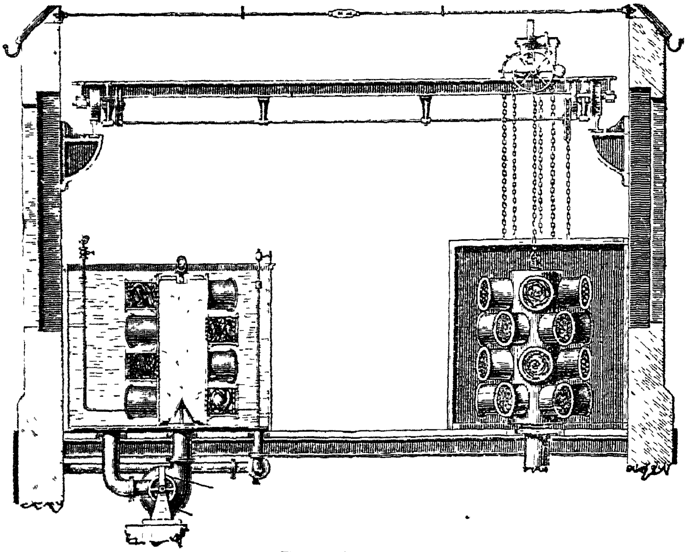


FIG. 463.

into a trough while the other half is covered, are fixed axial and peripheral rods, which keep the skeins taut. The wheel revolves slowly in the dye-bath, and the pegs, *b*, at the ends of the peripheral rods knock against an iron striker inside the trough, so that the rods revolve slightly each time; hence the skeins threaded on them are moved a few centimetres. Two workmen suffice for the charging and discharging of 100 to 200 kilos of wool

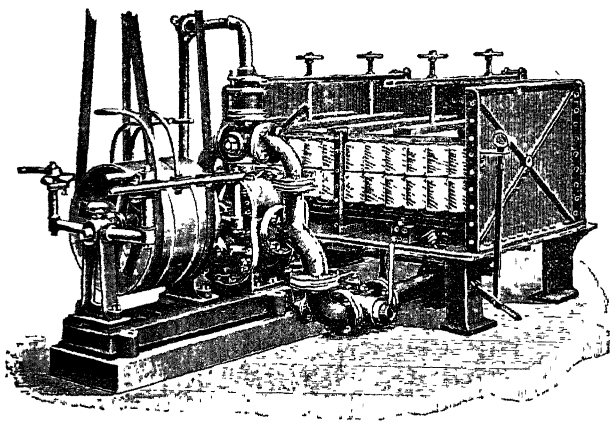


FIG. 464.

or cotton, while during the dyeing one man can look after three or four of these machines, adding the necessary colour now and then by means of the copper funnel *A*.

The steam for heating the bath reaches the bottom of the trough by the tube *d*. At *e* is an automatic indicator which shows when any particular peripheral rod does not turn owing to the skein being caught. The rapidity of revolution may be altered, but, as a rule, the movement is slow in order that the wool may not be felted.

In recent years a happy solution has been found to the problem of dyeing cotton or woollen yarn while still wound on the tubes of the spinning machine as spools or *cops*,

thus avoiding the winding into skeins and preserving the fibre better. At first the perforated tubes of the bobbins were inserted in drums which rotated in the bath and from the interior of which the air or liquid was pumped, the bath being hence circulated from the interior to the exterior of every bobbin and vice versa (Figs. 471, 472). There are various other arrangements, but recently a good reception has been everywhere accorded to an apparatus devised by De Keukelaeres of Brussels. This compresses the skeins or bobbins in a square iron or copper case on to a perforated false bottom, while, before the case is covered with a perforated metal plate, the yarn is covered with sea-sand, which is forced into all the pores of the mass not occupied by fibre by means of a water-jet. The cover is then fitted and screwed tight, and the bath circulated through the mass of yarn by means of a pump capable of developing considerable pressure; the liquid may circulate from bottom to top and vice versa and, finding no channels open, is obliged to traverse the fibre uniformly. When the dyeing is finished, it suffices to place the bobbins in a perforated basket and to shake this in a vessel of water to separate the whole of the sand, which collects at the bottom of the vessel and can be used again.

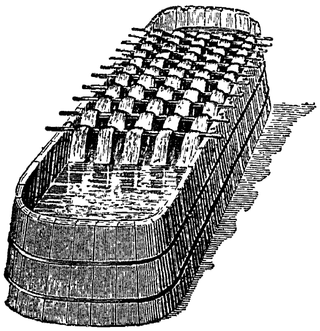


FIG 465.

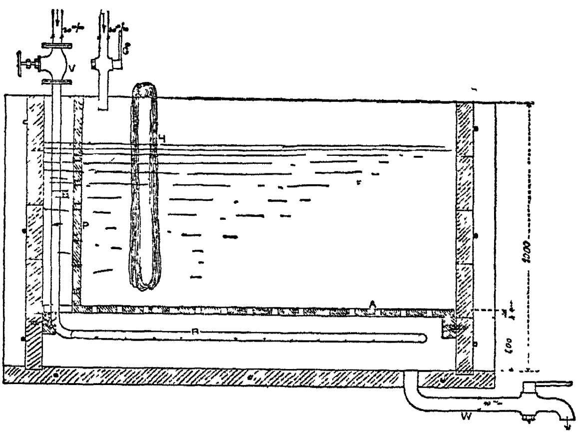


FIG. 466.

For dyeing skeins of cotton with Turkey red, which is the fastest red for cotton, the latter must be prepared and mordanted. It is not bleached with chlorine but is boiled for a long time with a caustic soda solution (0·75° Bé.) under pressure (2 atmos.) for 4 to 5 hours. When washed, the skeins of cotton are passed repeatedly into a bath of neutralised ammonium sulphoricinate (20 kilos of 50 per cent. strength per 100 litres of water; *see* p. 327); this operation is readily done with a suitable machine (Fig. 473), which is fitted with ingenious contrivances for pressing, wringing, untwisting, and immersing the skeins in the sulphoricinate bath repeatedly and automatically. When thoroughly soaked, the skeins are dried at 50° to 60°, then steamed under an excess pressure of 0·5 atmos. in an autoclave for an hour, and afterwards passed into the mordanting bath, consisting of a basic aluminium sulphate solution (7° Bé.) at 45° (with an iron mordant, a violet colour is obtained instead of red; with one of tin an orange colour, and with one of chromium a reddish brown colour; but these mordants are rarely used in practice); they are subsequently dried at 45°.

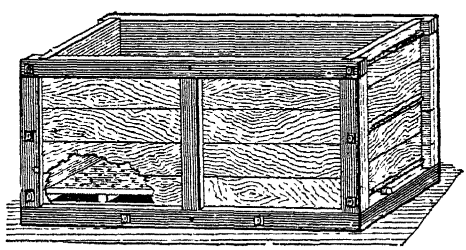


FIG. 467.

Use is often made next of a tepid bath consisting either of a little chalk suspended in water or of sodium arsenate, to remove any sulphoricinate not stably fixed, and hence to give subsequently a brighter colour. After this preparation, the skeins are passed into the dye-bath (10 to 15 per cent. of alizarin paste, calculated on the weight of cotton) contained in wooden vats and heated by tinned copper steam-coils ; the temperature is first kept at

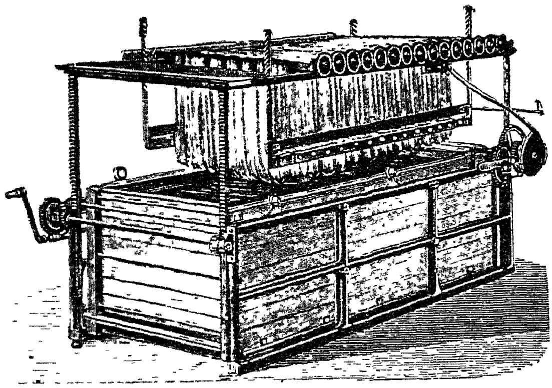


FIG. 468.

25° for an hour and is then raised in 30 minutes to 65° to 70°, the goods being manipulated for an hour. The dyed skeins are dried and are often introduced, without washing, into a second sulphoricinate bath, being then steamed for an hour in an autoclave at 1 atmos. ; the colour is not very bright but is made so by immersing the material for half an hour in a 0·5 per cent. soap solution heated under slight pressure (0·5 to 0·25 atmos.). Thorough

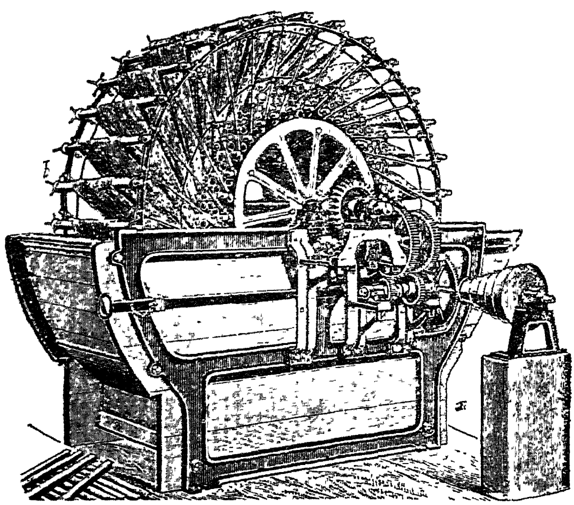


FIG. 469.

washing with water is followed by drying at a gentle heat. Although Turkey red is removed to a small extent if the material is scoured with a white fabric, yet it is the fastest red against washing and light now prepared on cotton. Kornfeld (1910) regards the fastness of Turkey red as due, not to the constitution of alizarin, but rather to the formation of a highly resistant double salt of aluminium oleate and the calcium salt of alizarin, and still more to the polymerisation of the fatty acid molecules under the action of steam.

According to a patent by Kornfeld, Turkey red dyeing may be carried out in the usual mechanical apparatus with circulation of the bath, the alizarin being rendered soluble by means of sucrate of lime.

Cotton Fabrics are sometimes dyed in ropes with vessels similar to those used for wool (*see later*), but more usually in the so-called *jigger* (Fig. 474), which is a rather shallow wooden trough provided with two outside rollers worked alternately by gearing so as to wind or unwind the pieces (3–4); the latter are sewn end to end and are kept quite taut, and pass below two small rollers close to the bottom of the trough. The dye solution in the bath may be heated at will by direct or indirect steam.

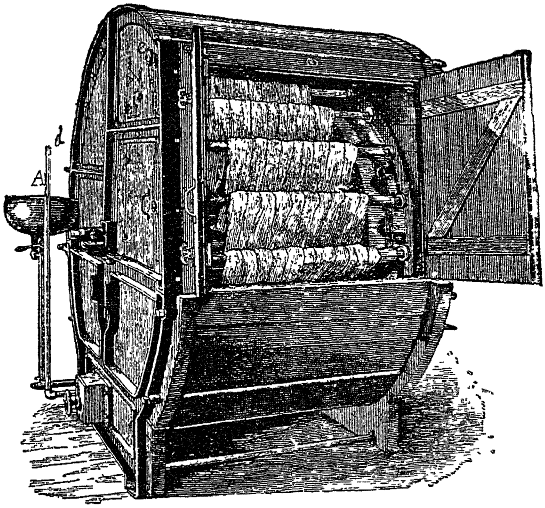


FIG. 470.

The jigger is often used also for dyeing *unions*, *i.e.* fabrics composed of cotton warp and wool weft, since these do not cockle or wrinkle, as all-wool goods would do, when passed under tension from one roll to another.

Woollens are usually dyed in wooden vessels provided with one or two reels which raise the goods in ropes from the front part of the vessel and drop them into the bath, the inclined wall at the back forcing them in folds on to the bottom of the vessel itself (Figs. 475, 476).

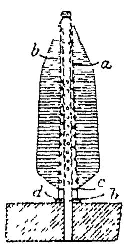


FIG. 471.

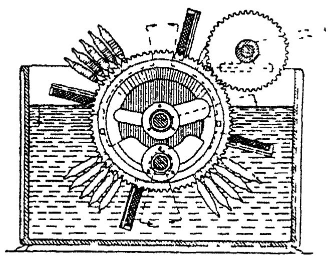


FIG. 472.

In some cases the velocity of rotation of the reels can be varied at will, being accelerated at the moment when the colour is introduced into the perforated compartment which admits of its gradual passage into the whole of the bath. The perforated steam-pipe also passes into the bottom of this compartment and is so arranged that the steam does not strike against the pieces, as this would result in irregular dyeing. The velocity of the reel must not be too high (20 to 50 cm. per second), as otherwise the wool would felt and the bath cool too rapidly. When the pieces are introduced into the vessel, one end is thrown over the reel and then stitched with twine to the other end (*see* Fig. 476). In some cases the materials (*e.g.* cashmeres) are twisted, by the movement in the trough, into very thin cords, into which penetration of the colouring-matter is difficult and irregular; in order

to avoid these disadvantages, such fabrics are first folded in two lengthwise and the selvedges then stitched together.

During the dyeing operation, the dyer cuts off small samples of the fabric from time to time, washes them, dries them in a warm towel and compares them with a specimen, so that fresh addition of colour may be made where necessary. Such fresh colour is dissolved apart in a wooden bucket in a few litres of the hot dye-bath, the solution being always

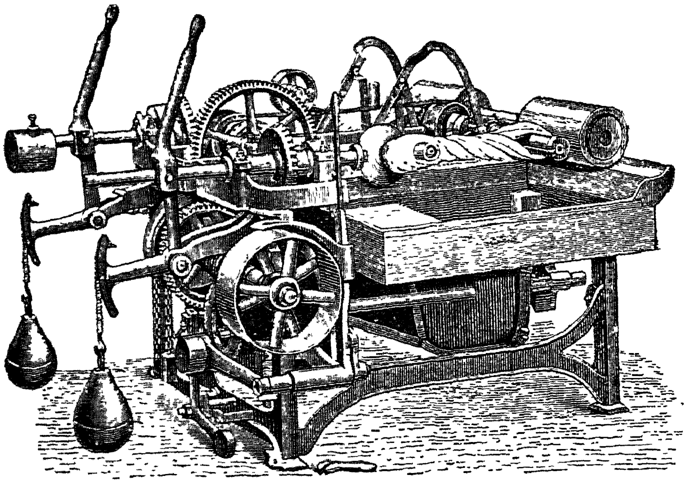


FIG. 473.

passed through a very fine hair-sieve to remove granules of undissolved dye, which would spot the material; the steam-cock is closed while the new dye is being gradually added.

The dyeing of woollen fabrics is commenced with a bath of tepid water (40° to 50°) with the addition of 10 to 15 per cent. of crystallised sodium sulphate and 2 3 per cent. of concentrated H_2SO_4 (or 5 to 6 per cent. of sodium bisulphate) (these proportions referring to the weight of the fibre). The colouring-matter (a few grammes for pale colours and as

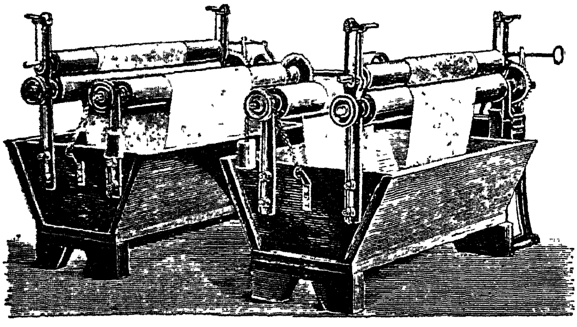


FIG. 474.

much as 5 kilos of black per 100 kilos of material) is added in several portions at the beginning of the operation, the goods being slowly moved meanwhile. In the course of an hour the bath is brought to boiling and this may last one or two hours before the dyeing is complete. Finally the steam-tap is shut and the goods discharged into a vessel of cold water.

After being rinsed and folded roughly by hand they are left to drip on beams for some time, a further part of their water being removed by two or three minutes' centrifuging (*see* p. 468). The goods are then ready to be dried in the apparatus described later.

When very delicate wool or wool and silk fabrics (with gathers and embroidery) are to be dyed, they are sometimes wound concentrically on hooks fitted to a frame such as that shown in Fig. 477. In this case the frame is only moved now and then, so that the fabric may not be injured.

Textile Fibres in Flock are dried in a series of superposed chambers with perforated bases on which the moist, centrifuged fibre is spread (Fig. 478, I). At II is seen a counterpoised elevator on which is placed the charged chamber ready to be introduced into its position in the series in place of one containing fibre already dried. The air used for the drying is forced in by the fan *A*, and is heated in the tubular steam heater *B*. The lower chambers are dried first, and when these are discharged, the remaining ones are lowered

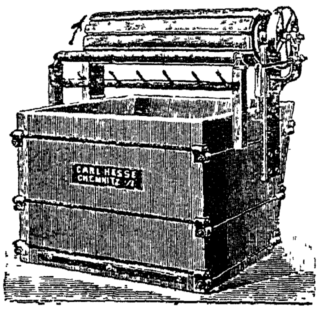


Fig. 475.

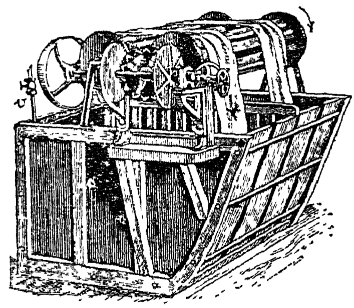


Fig. 476.

automatically and fresh ones introduced at the top. Yarn on bobbins or spindles can also be dried in these chambers.

Skeins of yarn may be dried by threading them, after centrifuging, on rods and fixing these horizontally in frames in a chamber heated by branched steam-pipes on its base; the moist air issues from vent-holes fitted to the ceiling. In some cases the yarn is dried in hot chambers, the skeins being stretched over revolving reels furnished with central steam-pipes, as is shown in Fig. 479.

Good results are also obtained with the continuous drying machine, in which the skeins are placed on rods, &c., carried by chains moving in a drying chamber (Fig. 480) supplied

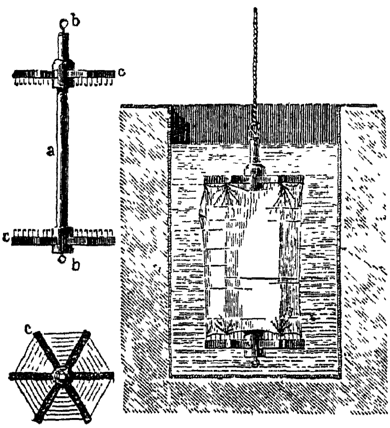


Fig. 477.

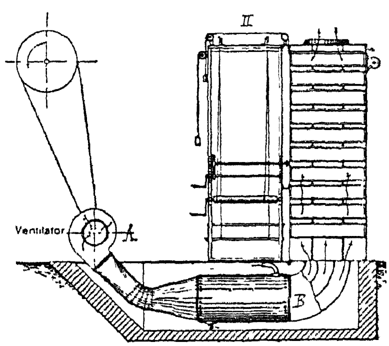


Fig. 478.

at *A* with hot, dry air. The dry yarn issues continuously at *Z*, while the moist air finds an outlet at *B*.

Fabrics as they come from the centrifuge are usually dried by passing them, well stretched, over a battery of seven or nine copper drums *F* (Fig. 481). These are all moved regularly by gearing, the rate being regulated by means of the large disc *B*, which is actuated at a point more or less distant from its centre by the friction roller *C*; the latter is turned by the pulley *A*, joined by belting to the general system of power transmission.

The dried fabrics are then examined throughout their entire length and breadth before a well-lighted window in order to ascertain if there are any defects in dyeing or otherwise, so that these may be remedied before dressing.

Dressing of Fabrics is effected by impregnating them with solution of gum, bone glue, starch, &c. The fabric is passed beneath a roller dipping into a vessel containing the solution, and is then pressed by a second roller superposed to the first in a kind of *foulard* like that shown in Fig. 482; the vessel may have the section shown in Fig. 483. The gummed fabrics are subjected to mechanical treatment varying according to the type required. Dressing increases the strength and weight of the tissue, which is next dried and at the same time pulled out both lengthwise and breadthwise in order to bring it back

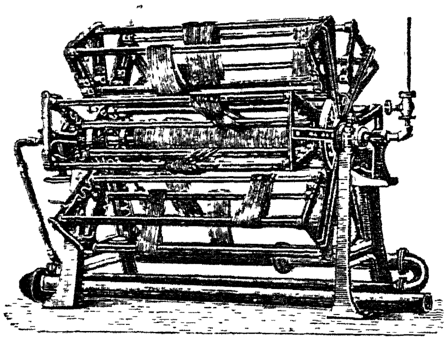


FIG. 479.

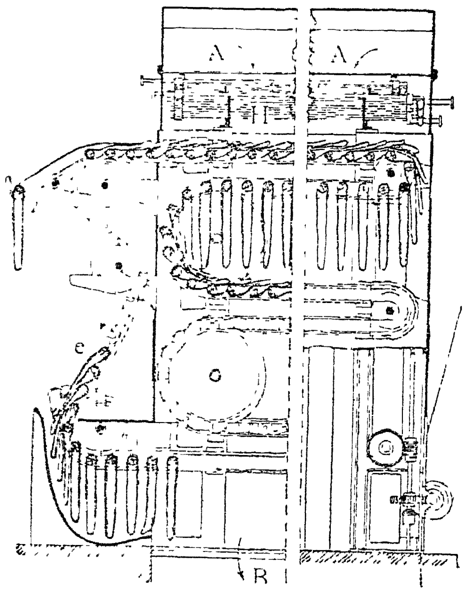


FIG. 480.

as nearly as possible to the dimensions they possessed before dyeing. This is effected by means of the so-called *tentering frame*, into which the tissue passes, fixed laterally by the selvedges on two chains carrying clips or needle-points; the distance between the two chains is gradually increased to the desired width, which is shown on a graduated iron

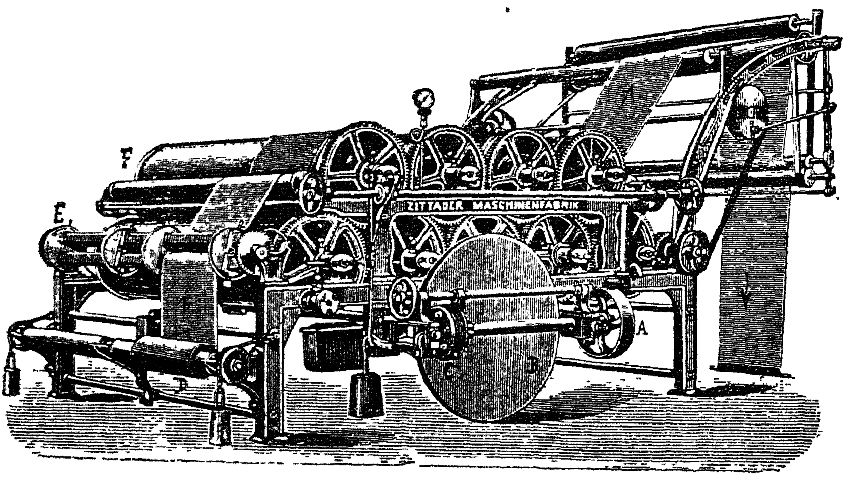


FIG. 481

bar, *A* (Fig. 484). Fig. 485 shows a complete frame with the gumming machine *B* and two operatives fixing the selvedges on the points of the chains. The widened cloth is dried throughout its whole length by a current of hot air blown into a long chamber beneath, and finally by a heated drum, *C*. These frames are 8 to 12 metres long, but are sometimes constructed on several stories in order to save length. Fig. 486 gives a better view of the frame in outline: the gummed, centrifuged, and folded cloth lies ready on the two benches,

B; the air is heated at *T* and the fan *V* forces the hot air into the long chamber, *R*; the cloth enters at *B* and issues at *C*.

Milled fabrics and certain others which are required to present a hairy surface are passed to the so-called *raising gigs* (Fig. 487), consisting of one or more large drums carrying numbers of metallic points or strings of the spiny capsular heads of *Dipsacus fullonum* (10 to 20 cm. in length, Fig. 488) on spindles. The drums or spindles revolve so that the

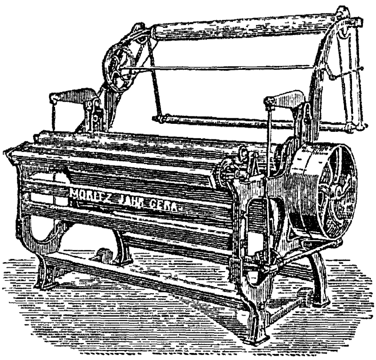


FIG. 482.

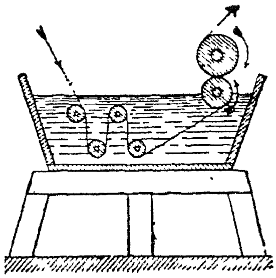


FIG. 483.

points just touch the stretched surface of the cloth and draw from it fairly long hairs, which are then rendered uniform by passing the dry cloth to the cutting and brushing machines furnished with cylindrical brushes and with drums fitted with cutting edges arranged helically (*see* Fig. 489); the first brush, *A*, raises the hair, the cutter, *B*, cuts or crops it off uniformly, and the second brush, *C*, sets it regularly all in the same direction.

A similar operation is carried out with velvets, which are, however, woven specially, and often in two superposed pieces attached by a large number of fibres, which are then cut exactly in two so as to give two separate pieces each with a hairy face.

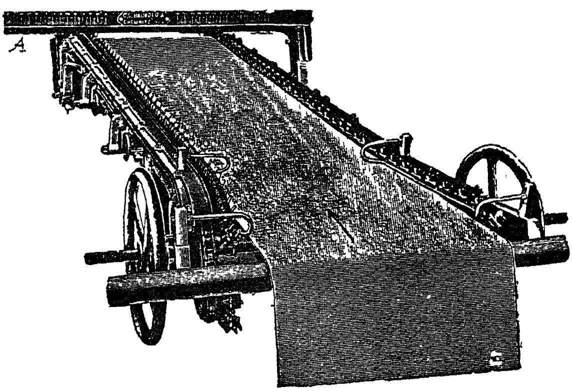


FIG. 484.

When the fabrics are required to have a very smooth, shiny surface, they are passed after gumming to the so-called *calenders*. A common type of the latter for wool and unions, which require but little pressure, is that shown in Fig. 490: the cloth is seized by the selvedges by two discs fitted with bands, *A* (called a palmer), which enlarge the cloth to the required size and then pass it on to a continuous felt, *C*, which transfers it in a well-stretched and compressed condition on to a copper drum, *B*, heated by steam under slight pressure. For cotton or cotton and silk fabrics, use is made of calenders with several superposed and heated cylinders to which pressure may be imparted by means of suitable levers (Fig. 491) in such a way as to exert a kind of friction on the cloth passing from one cylinder to the other. When a very high finish is required on certain *satin* fabrics of cotton, they are passed between two massive steel cylinders which are under very high pressure

(hydraulic) and one of which is fluted with very fine striations (as many as 10 to 25 per millimetre, as suggested by Schreiner); these leave their stable imprint on the fabric like so many minute, shining cylinders like silk fibres, which reflect light under any angle;

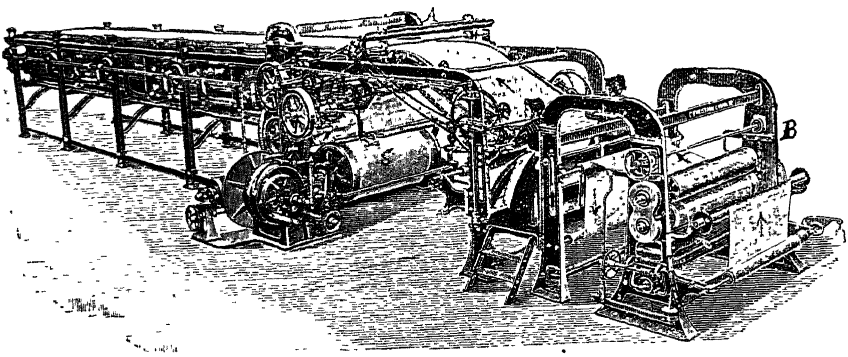


FIG. 485.

this finish is known as *silk finish* (or Schreiner finish). Similar calenders are used for obtaining special watered effects (*moiré*).

On woollen fabrics calenders generally produce a so-called false finish like that of a bright sheet of metal. This is not regarded as desirable by the merchants, and, further,

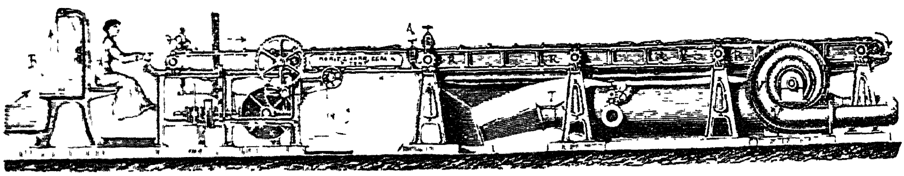


FIG. 486.

such a finish will show rain-drops, even after drying. In order to avoid this inconvenience and the better to fix the material in both directions, so that it will not shrink when worn, it is subjected to so-called *steaming*, *i.e.* to the action of steam under a pressure of 2 to 3 atmos. (some colours will not withstand this operation). The fabric is well stretched

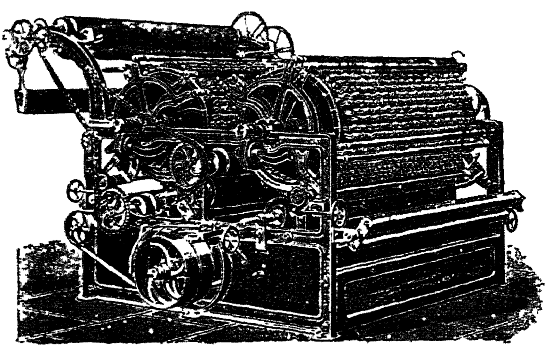


FIG. 487.

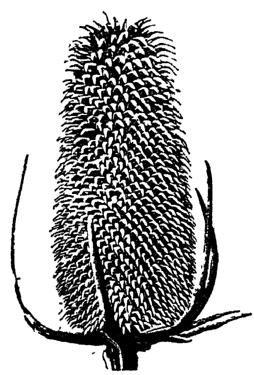


FIG. 488.

and wound, together with a cloth, round a perforated cylinder; the roll of two or three pieces thus obtained is wrapped in cloth fastened by strings, the cylinder being then fixed vertically on a steam-cock (Fig. 492). The steam, under pressure, is obliged to traverse the whole of the roll of fabric, and when it issues in a dense cloud (after a few minutes) the operation is at an end; the roll is then removed, but is allowed to cool without unrolling,

since in that way it acquires a better and more resistant lustre. The latter is also found to be improved by carrying out the steaming in a vacuum, the rolls *G H* (Fig. 493) being introduced into a kind of horizontal jacketed autoclave, *X*, previously heated by passing steam through

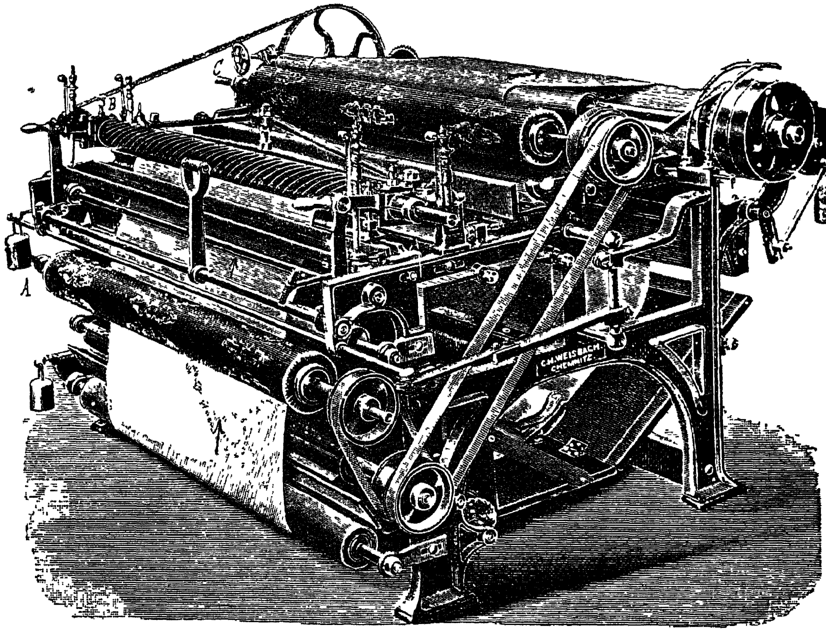


FIG. 489.

the jacket; when the cover *L* has been tightly closed, the autoclave is evacuated by passing steam into it and condensing the steam by a water-spray in the cylindrical chamber *W*, which communicates with the autoclave by means of the tap *R*. After this the steam is passed through the roll of fabric, either from the inside to the outside or vice versa, by fixing the roll in a suitable manner to the steam-cock.

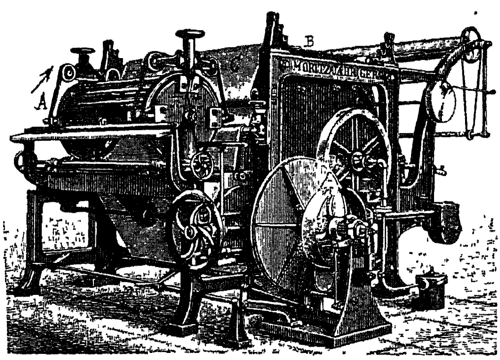


FIG. 490.

Of the various other operations comprised in the finishing of fabrics, only that of *pressing between hot card* need be referred to; this gives lustre to cloths which are not subjected to steaming and in general imparts a very soft, pleasant feel, more particularly to the finer woollens.

In this operation, which is the last of importance, the best effect is obtained when 10 to 15 per cent. of moisture is present, so that fabrics which are too dry are treated first with a slight steam-jet, being meanwhile wrapped on drums in large rolls; after some

hours these rolls are unwound and the fabric arranged in regular folds, between each adjacent pair of which is inserted a piece of hot, smooth card. The whole is then left

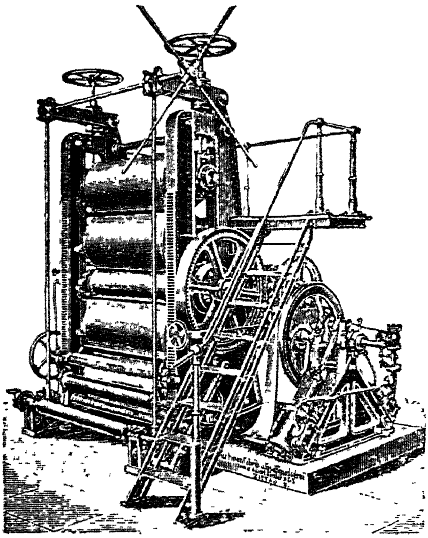


Fig 491.

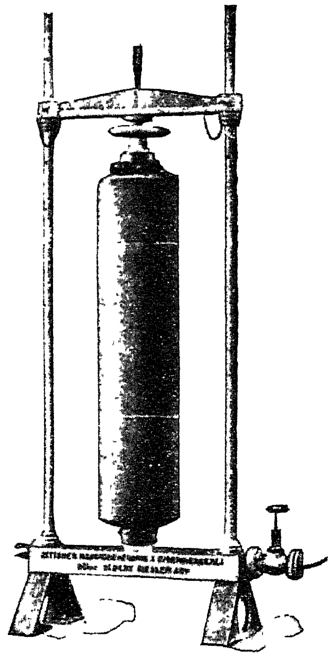


Fig. 492.

under pressure in a hydraulic press (Fig. 494) for 10 to 12 hours. In order to obtain uniform heating while the pressure is being exerted, presses are now used with double pillars in which steam circulates (Fig. 495); also the pillars are sometimes heated electrically.

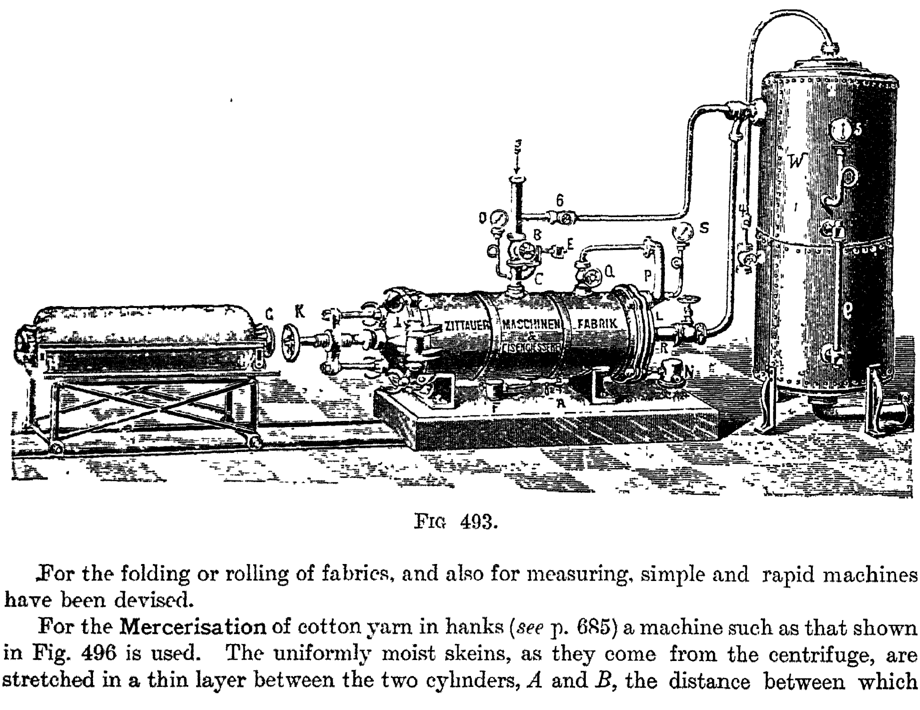


Fig 493.

For the folding or rolling of fabrics, and also for measuring, simple and rapid machines have been devised.

For the **Mercerisation** of cotton yarn in hanks (*see* p. 685) a machine such as that shown in Fig. 496 is used. The uniformly moist skeins, as they come from the centrifuge, are stretched in a thin layer between the two cylinders, *A* and *B*, the distance between which

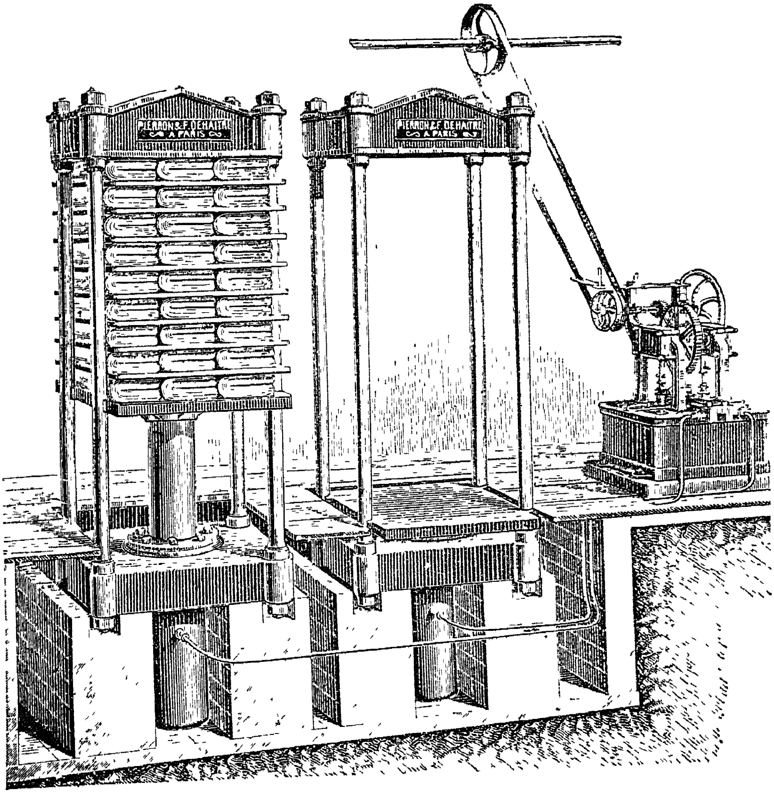


Fig. 494.

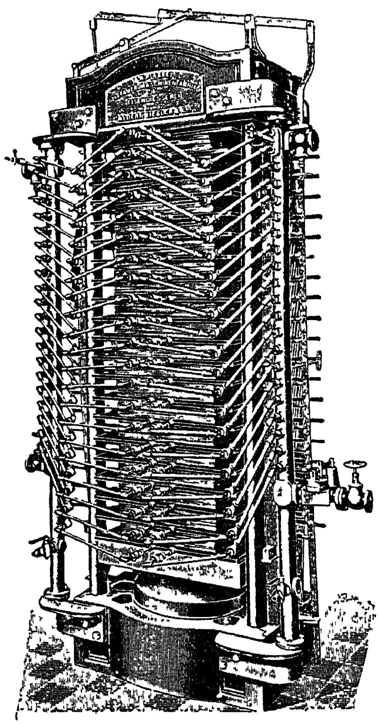


Fig. 495.

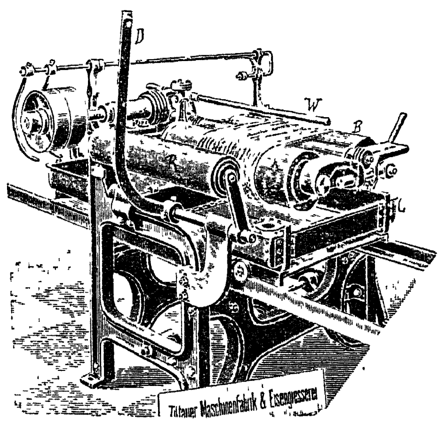


Fig. 496.

can be increased so that the skeins are considerably stretched. Then, when the rollers are revolving, a lever is operated to raise the iron vessel, C, containing cold caustic soda solution of 25° to 30° Bé., one-half of each cylinder dipping into the soda. At the end of a few minutes the imbibition is complete, the soda solution is drawn off into a tank provided with a pump, while a copious supply of water is sprayed on to the skeins, which are pressed by the roller R. When washing is complete, the tension is relieved and the skein removed.

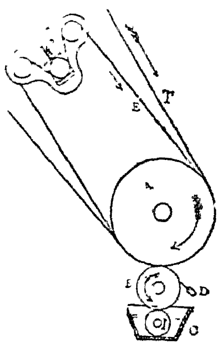


FIG. 497.

There are also other machines for mercerising fabrics, these being kept stretched by contrivances similar to those used in the tentering frame (*see* Figs. 484 to 486), while the caustic soda is removed from the fabrics by means of suction pumps. The fabric is then washed with a little hot water so as to give a moderately strong solution of caustic soda, which may be used to dissolve solid caustic soda or may with advantage be concentrated in multiple-effect evaporators (*see* vol. i, p. 442). The caustic soda is removed completely from the fabric by thorough washing in cold water, then in a slightly acid bath and finally in water.

The **Printing** of textiles, as indicated on p. 707, is carried out by pressing, with a

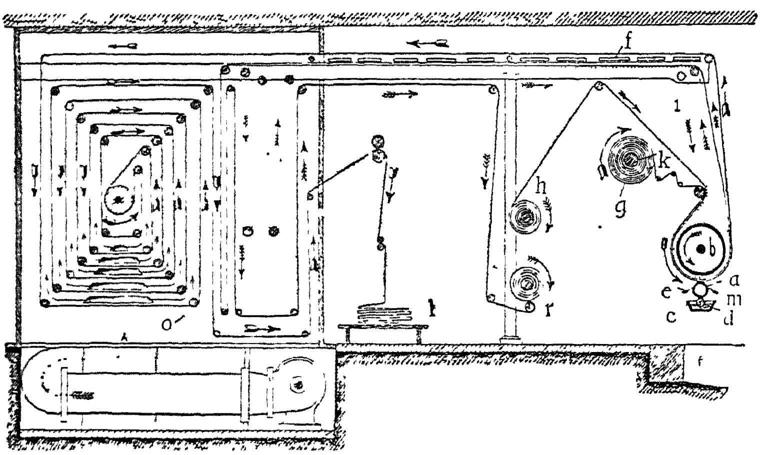


FIG. 498.

rubber roller, A (Fig. 497), the fabric or yarn against a copper cylinder, B, on which the design is engraved. The copper cylinder receives the pasty colour from a roller, I, dipping into the vessel, C, containing the thickened colour solution, a blade, D, then scraping away the excess of colour so that only the hollows of the design remained filled. Between the rubber cylinder and the fabric, T, to be printed runs a continuous band, E, which is kept taut by the contrivance V. The arrangement used, with the adjacent drying chamber, o, is shown in Fig. 498: the vessel of colouring-matter is at cd, and the fabric is unwound from g together with the accompanying cloth h, and the continuous pressure cloth i; the dyed and dry fabric is collected in folds at l, while the cloth h is rewound at r, and i returns constantly to the printing cylinder. When several colours are to be printed on one and the same fabric, a number of rolls and colour vessels are required, as is shown diagrammatically in Fig. 499.

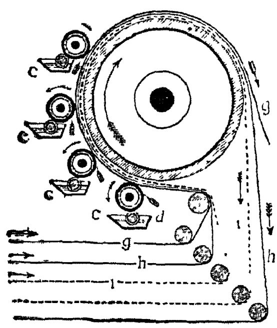


FIG. 499.

Fig. 500 shows a complex machine for the printing of textiles in twelve colours at once; highly skilled workmen are required to regulate its working with accuracy.

A simple arrangement for printing yarn in skeins by hand is shown in Fig. 501. The skeins are kept taut between the rods *A* and *B* and the printing rollers, which are not very clear in the figure, are below *A*. The printed skeins are hung on rods fitted to a framework, this being introduced into an autoclave to be treated with steam under pressure (Fig. 502).

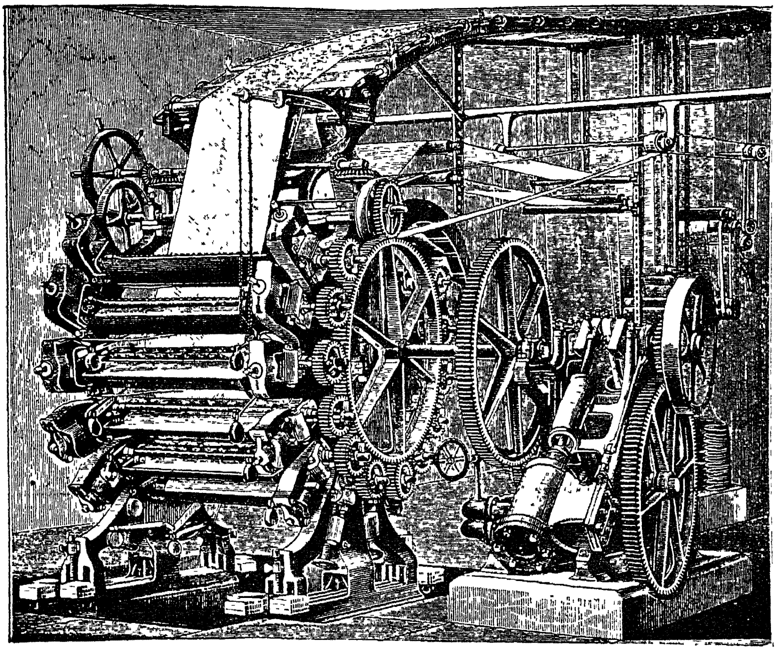


FIG. 500.

Printing colours are boiled with the thickening agents in suitable double-bottomed boilers, heated by means of steam and furnished with stirrers. Fig. 503 shows a battery of such colour-pans.

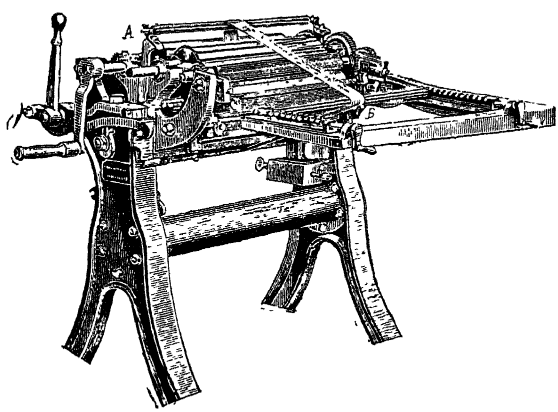


FIG. 501.

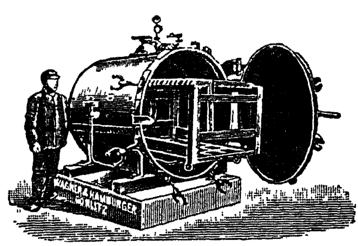


FIG. 502.

When mention was made of *aniline black* (p. 662), it was stated that the complete development of this colour is obtained in an oxidation chamber (Fig. 504). In the case of yarn, the method of continuous drying illustrated in Fig. 480 (p. 724) gives good results. But with fabrics use is generally made of a chamber with revolving rollers, where the fabric

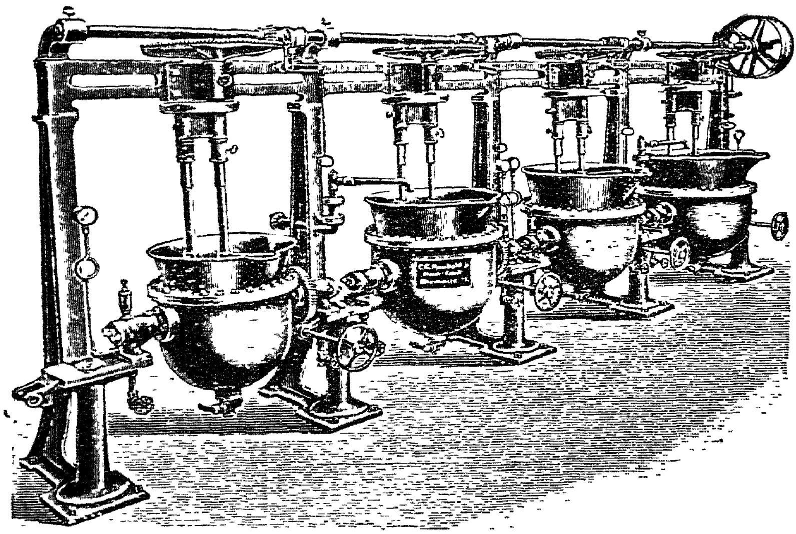


Fig. 503.

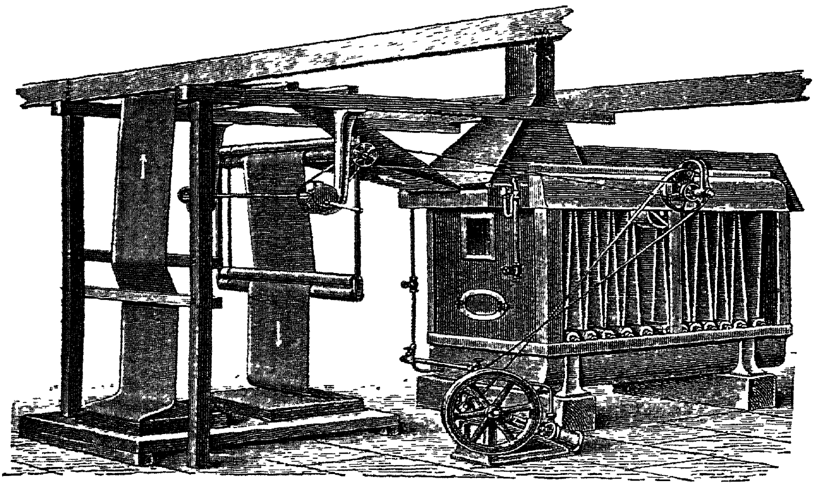


Fig. 504.

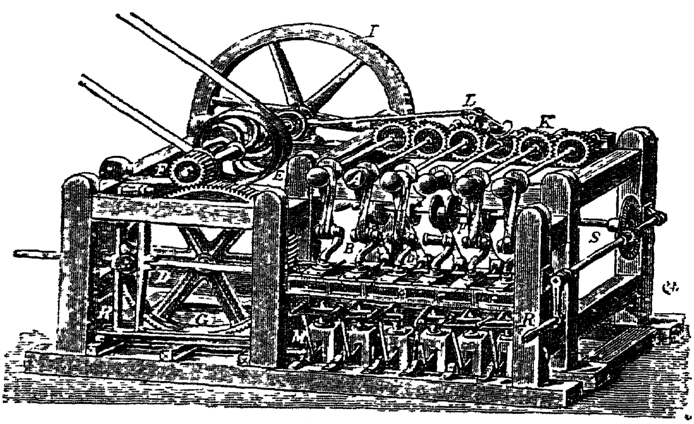


Fig. 505.

traverses slowly a very long path and issues completely black ; a hood is arranged to carry off acid vapours. Of great importance in this operation is the regulation of the temperature, of the draught and of the velocity with which the fabric passes through the chamber. Unexpected stoppages are dangerous, as they may lead to corrosion of the fabric or alteration of the colour.

To *polish* and *soften* silk, the skeins are stretched, twisted, and rubbed repeatedly on a smooth rod fixed in the wall. But nowadays this is done by machines (Fig. 505), which act automatically and give a large output.

T. PROTEINS OR ALBUMINOIDS

These are fundamental products in the formation and constitution of animal and vegetable organisms. The protoplasm of vegetable and animal cells, which is the origin of the metabolic processes and hence of the life of the organism, consists of protein substances, which are also indispensable components of foodstuffs.

From a physiological point of view they are therefore of the utmost significance, but their chemical nature is very complex and is still little understood, although the investigations of Emil Fischer and a number of able collaborators during the past ten years have to some extent pierced the veil surrounding this most important group of organic compounds, which had been previously studied, as regards some of their more superficial characters, by Ritthausen, Hoppe-Seyler, Hammarsten, Neumeister, Pflüger, Hedin, Küster, Nencki and Sieber, &c.

The numerous substances comprised in this group are all composed of C, H, O, N, and S, with, in a few cases, P ; their percentage compositions vary between the following limits : C, 50 to 55 ; H, 6·9 to 7·3 ; O, 19 to 24 ; N, 15 to 19 ; S, 0·3 to 2·4.

The molecular magnitudes of these substances cannot be established with certainty, since it is not easy to isolate single individuals, only very few of them crystallise, none are transformable into vapour, and in no case are true solutions obtainable capable of cryoscopic or ebullioscopic measurement ; their solutions are colloidal. Direct or indirect attempts to determine their molecular weights have given numbers varying from 10,000 to 30,000.

Both the sulphur and the nitrogen occur in two groupings, being partly removed by hot potash and partly more stably combined.

Absolute alcohol coagulates proteins and precipitates them to some degree unchanged from their aqueous solutions. They are also precipitated unaltered by solutions of sodium chloride, magnesium sulphate or ammonium sulphate of different concentrations, which are characteristic of the various proteins.

Proteins are coagulated and precipitated from their aqueous solutions by small quantities of mineral acids (nitric acid may be in excess). They have a feeble acid character and form salts as insoluble precipitates with metallic salts, *e.g.* ferric chloride, acidified mercuric chloride, copper sulphate, &c., and they dissolve small amounts of freshly precipitated ferric hydroxide. From these metallic precipitates proteins are liberated in a changed form.

Less pronounced is their basic character (like the amino-acids, they behave as both acids and bases at the same time), although egg-albumin is completely precipitated by weak acids, such as tannin, phosphotungstic acid, and picric acid.

Aqueous solutions of the proteins are coagulated on heating to different characteristic temperatures, and the coagulated proteins dissolve only in an excess of acid or alkali in the hot, their constitution being modified thereby and H_2S and NH_3 sometimes evolved : with alkalis they form albuminates and with acids, **Acid-Albumins** (*syntonins, see* p. 737), both insoluble in water and reprecipitable by neutralisation. By the protracted action of these two

reagents (**Hydrolysis**, *see below*) or by the action of pancreatic juice, which contains **Tryptase** (*see* p. 112), they yield various amino- or diamino-acids: glycocoll, alanine, phenylalanine, aspartic acid, glutaminic acid, leucine (in abundance), pyrrolidinecarboxylic acids, tyrosine, serine, triaminotrihydroxydodecanoic acid, β-indoleacetic acid, arginine, lysine, ornithine, tryptophane, cystine (sulphur compound), &c., all of them optically active with the exception of glycocoll. When a piece of boiled egg-albumin is heated at 37° with gastric juice, it rapidly dissolves with formation of **Peptones** and **Albumoses**. The peptones, passing into the intestines, undergo further hydrolysis, and as final products yield amino-acids. The complete hydrolysis of the albumin may be effected more rapidly by means of a concentrated acid (*e.g.* HCl), which gives amino-acids and also ammonia. By putrefaction various other substances are formed: **Ptomaines**, such as cadaverine (*see* p. 214), putrescine or tetramethylenediamine, &c.; glucosamine, methylamine, ammonia, β-indoleacetic acid, phenylacetic acid, carbonic acid, hydrogen sulphide, formic to caproic acids, partly of normal structure and partly optically active (valeric and caproic), &c.; indole, skatole, phenol, cresol, mercaptan, methane, &c., all of these being oxidation or reduction products of the original compounds obtained. The action of pathogenic bacteria on proteins yields poisonous substances, the **Toxalbumins**, which are similar in composition to the proteins and lose their toxicity when their aqueous solutions are heated.

The following *reactions* are characteristic of the proteins:

Protein solutions give a violet coloration (like biuret) with alkali and a few drops of 2 per cent. copper sulphate solution (*biuret reaction*).

With nitric acid in the hot and even in excess a yellow precipitate is formed (*xanthoprotein reaction*).

With Millon's reagent (*see* p. 704) a red coagulum is formed on boiling.

The degradation or *hydrolysis* of proteins, when it is complete and takes account of all the more or less complex groups composing the protein molecule, will permit of an attempt, with probability of success, to synthesise these substances completely. Such more or less gradual decompositions are attained by protracted heating (for different times with different proteins and in some cases for 200 hours) in an autoclave, or by means of soda or baryta (Schützenberger), or, better, 25 per cent. solutions of hydrochloric or sulphuric acid. But even under these conditions some of the intermediate compounds cannot be detected, the hydrolysis being in many cases too rapid. Hugounenq and Morel (International Congress of Applied Chemistry, London, 1909) have obtained a somewhat more gradual hydrolysis by using 15 to 25 per cent. hydrofluoric acid solutions and heating for 100 to 150 hours.

The separation of the numerous amino-acids resulting from the hydrolysis of the proteins constitutes a difficult problem, which has recently been solved by E. Fischer for the amino-acids and by Kossel for the diamino-acids. Fischer subjects the esters of the amino-acids to fractional distillation *in vacuo* and thus determines their separate amounts.

It is thought that the amino-acids occur in the proteins in a condensed form similar to **Glycylglycine**, $NH_2 \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$. Indeed Fischer was able to synthesise the so-called **Polypeptides**, which contain such groups and in many respects resemble the natural peptones derived from proteins (*see later*); the esters of the amino-acids readily give up alcohol and undergo ketonic condensation to polyanhydrides, and these, under the influence of alkali, take up a molecule of water, giving the peptides:

$$\underset{\text{Ethylglycocoll}}{2NH_2 \cdot CH_2 \cdot CO_2C_2H_5} = 2C_2H_5 \cdot OH + \underset{\text{Double Anhydride or Diketopiperazine}}{NH{<}\begin{matrix} CO \cdot CH_2 \\ CH_2 \cdot CO \end{matrix}{>}NH} \text{ (and this} + H_2O)$$

$$\longrightarrow NH_2\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2H.$$
Dipeptide or Glycylglycine

By chlorinating the carboxyl of the dipeptide with PCl_5 in acetyl chloride solution, a second molecule of ethylglycocoll may be caused to react with formation of a tripeptide, and so on, higher polypeptides similar to the natural ones being ultimately obtained,

$$X\cdots CO\cdot Cl + NH_2\cdot CH_2\cdot CO_2\cdot C_2H_5 = HCl + X\cdots CO\cdot NH\cdot CH_2\cdot CO_2\cdot C_2H_5\,;$$

these polypeptides are completely hydrolysed by hot concentrated HCl, are digested by tryptase, withstand cold alkali, are soluble in water and insoluble in alcohol, and give the reactions of the proteins (*see below*) These syntheses, which represent the first small step towards the synthesis of the proteins, give an idea of the enormous difficulties to be overcome before the natural proteins can be reconstructed. Indeed, since the dipeptides have molecular weights of about 100, while with the proteins the molecular weight certainly exceeds 10,000, at least 100 of these groups must be present. Also, as several of the amino-acids contain one or more asymmetric carbon atoms, stereoisomerism is possible, and so likewise is tautomerism, *e.g.*

$$—HN\cdot CO— \rightleftarrows —N:C(OH)—$$

The investigations of Fischer have resulted in the synthetical preparation of more than a hundred of the simpler polypeptides, the highest of which is an octadecapeptide; but on ascending the series the complications and difficulties increase disproportionately. This problem could occupy a whole generation of chemists, and its solution would be a glorious triumph for the twentieth century, as it would banish for ever the Malthusian threat that one day humanity will be starved owing to the disproportion between the population and the productive capacity of the earth. Indeed, while it is not possible to replace the proteins in human nutriment by fats or carbohydrates—these alone leading to rapid decay of the organism and to death—proteins of themselves are able to supply all the needs of the organism. So that the insufficient production of proteins in nature at some future time would of a certainty be accompanied by famine, unless a method of synthesising proteins by chemical means had previously been discovered. Berthelot imagined that one day the air would supply the oxygen and nitrogen, and water the hydrogen for this synthesis. And it is not for us to deny that the dream of yesterday may become the reality of to-morrow, if chemistry learns how to imitate the simplicity and economy of the natural synthetical processes best exemplified in plants, which from carbon dioxide, water, and nitrates are able to effect continuous production of carbohydrates, fats, and proteins. Our laboratory synthetical methods are still too cumbersome, too indirect, and generally too costly. Only when the action of catalysts and light and the laws of colloids have been more closely studied can any hope be entertained of a more rapid progress in the synthesis of such complex organic substances.

The numerous different proteins are usually classified in the following groups and sub-groups:

I. NATURAL PROTEINS

(1) ALBUMINS (of eggs or **Egg-albumin**, of blood serum or *serum-albumin*, of milk or *lactalbumin*, of muscles, of plants, &c.).

These are the most common and also the best known of the proteins, since they can be isolated as definite, crystalline, chemical individuals. They are soluble in water, dilute acid or alkali, or *neutral* solutions of NaCl, $MgSO_4$, or $(NH_4)_2SO_4$ (the globulins being

insoluble), but in acid solution these salts precipitate the albumins. In the hot they are coagulated.

The products of the putrefaction of albumin contain also *p*-**Hydroxyphenylacetic Acid**, $OH \cdot C_6H_4 \cdot CH_2 \cdot CO_2H$, which occurs likewise in urine (acicular crystals coloured greenish by ferric chloride).

There exists nowadays a considerable trade in dry albumin obtained from the egg and from blood. In various countries, egg-yolks [1] are preserved in salt and employed in different industries (for tanning, making lecithin, culinary purposes, &c.), and the fresh white separated is diluted with a little water, beaten until it forms a froth, allowed to stand until the latter is destroyed, filtered through woollen bags, and evaporated in a stream of air at 30° to 40° in large shallow pans; after 40 to 60 hours there remains a thin, yellowish, transparent pellicle, which is completely soluble in water and keeps without developing any unpleasant odour.

From fresh blood (from the butcher's) pure albumin is separated with greater difficulty. The blood is first allowed to undergo spontaneous coagulation, the blood globules and other impurities thus collecting in a compact mass so as to allow of the ready decantation of the faintly coloured liquid serum containing the albumin; or, after coagulation, the blood may be introduced immediately into a centrifugal separator (*see* p. 395). The centrifuged or decanted liquid is beaten (without dilution), filtered, decolorised with charcoal, and dried as above. In many cases decolorisation is difficult, and the albumin has to be precipitated with lead acetate; the decanted precipitate is washed and suspended in water, which is then saturated with carbon dioxide, the lead carbonate being allowed to settle. The clear albumin solution is treated with a little hydrogen sulphide, which removes traces of lead, and filtered, and the pure solution evaporated as with egg-albumin.

According to Ger. Pat. 143,042, the serum-albumin is coagulated by means of salt, dissolved in ammonia and treated at the boiling-point with hydrogen peroxide, the excess of ammonia being subsequently driven off. The method described in Eng. Pat. 10,227 (1905) consists in treating the serum successively with hydrosulphite, acetic acid, and sodium acetate, the liquid being then neutralised with ammonia and evaporated as usual.

Albumin is used in various industries: for photographic papers, in textile printing, in printing titles in gold-leaf on books, as a clarifying agent in wine-making (*see* p. 156), &c.

Egg-albumin costs, according to its degree of purity, £24 to £28 per quintal. Blackish blood-albumin is sold at 48*s*. to 60*s*. per quintal, the dark at 88*s*., the pale at £5 to £8, and the pale powdered at 128*s*. to 208*s*.

(2) **GLOBULINS** (of plants or **Phytoglobulins**, **Serum-globulin**, **Lactoglobulin**, &c.) are insoluble in water but soluble in dilute acid or alkali. At 30° they are precipitated

[1] The *eggs* produced by different breeds of hens are of varying size and weight (from 45 to 65 grms; duck, goose, and turkey eggs weigh from twice to four times as much) and are composed of about 60 per cent. of white, 30 per cent of yolk and 10 per cent of shell (mainly calcium carbonate); the white contains 86 per cent. of water and 13 per cent. of albumin, and the yolk about 51 5 per cent of water, 28 5 per cent of fats, 15 8 per cent. of proteins (principally vitellin), 2 per cent. of salts, 0 45 per cent of cholesterol, 1 2 per cent. of phosphoglyceric acid, and 0·4 per cent. of extractive substances. As regards its nutritive value, an egg weighing 60 grms is equivalent to 50 grms. of meat, while its heat value is about 80 calories. Continuous evaporation of water takes place through the shell of the egg, and the volume of the contents diminishes, leaving a free air-space—varying in size in different eggs—which may be observed by looking through the egg at a candle flame in a dark chamber. Fresh eggs are also distinguishable from stale ones by the specific gravity: fresh eggs sink in a salt solution of sp gr. 1·078, those 2 to 3 weeks old in one of sp. gr. 1·060, those 3 to 5 weeks old in one of 1 050, and rotten eggs in one of sp. gr. 1·015. It has also been observed that fresh eggs float horizontally on a denser liquid, those 4 to 6 days old at an angle of 20°, those 8 to 10 days old at an angle of about 45°, and those 15 to 20 days old at an angle of 60°.

The *preservation of eggs* is of considerable importance, since in summer eggs are abundant and cheap, while in winter they are scarce and cost double as much A common means of preservation formerly employed consisted in immersing the eggs in water saturated with lime (which partially filled up the pores of the shell with calcium carbonate), but in this way they acquire an unpleasant taste; an improvement is effected by adding 5 per cent. of sodium chloride to the lime water Others preserve them in pounded salt or in salt and bran, pointed end down, while others again smear them with wax, vaseline, and oil or tallow. Large quantities of eggs are now preserved for some months (May to November) by placing them in thin layers on wooden lattices in cold chambers, which are kept at a temperature of 1° to 2° and a humidity of 70° to 80°, and are well ventilated, preferably by means of an apparatus producing ozonised air. In certain cases good results are obtained by preserving the eggs in 10 per cent. sodium silicate solution, although such eggs often burst during subsequent boiling. A mere coating of the silicate or of collodion is of little avail. For transport eggs are arranged in layers, with alternate layers of old straw, in wooden boxes.

It is estimated that Italy produces from 5,000,000,000 to 6,000,000,000 eggs (about 60,000,000 being hens' eggs) and the exportation, which in 1905 exceeded 320,000 quintals, worth about £1,800,000, fell to 228,500 quintals in 1907, a large part of the English market (to which France sends more than 1,000,000,000 eggs) and also of the German market (captured by Russia and Denmark) being lost.

unchanged, completely by solutions of ammonium or magnesium sulphate and partly by sodium chloride solution. Their solutions are coagulated by heat.

(3) **NUCLEO-ALBUMINS (Vitellin, Casein, &c.)** are acid in character and decompose carbonates; they are slightly soluble in water, but dissolve with formation of salts in caustic soda or ammonia and are then coagulated neither by heat nor by alcohol. They contain phosphorus (0·85 per cent. in casein) but are distinct from the nucleo-proteins, which give xanthine bases among their decomposition products. **Casein** is found in milk (*see* p. 385) and is coagulated by rennet or by dilute acids at 50°; it is soluble in borax or potassium carbonate and is rendered insoluble by formaldehyde. Converted into salts in various ways, it is placed on the market as a concentrated and readily digestible food (*plasmon, nutrose, tropon,* &c.); it is mixed with mineral colouring-matters to make varnishes. The hydrolysis of casein yields various amino-acids and complex tribasic acids (Skraup). *Vegetable caseins* are also known.

To obtain pure casein in the laboratory, diluted skim-milk to which 0·5 per cent. of acetic acid has been added is heated to 55° to 60° and the precipitated casein collected on cloth, washed well with water, redissolved in very dilute ammonia, decanted or filtered to remove the undissolved fat and nuclein and then reprecipitated with acetic acid as at first. It is again collected on cloth, washed with alcohol and then with ether, and dried in a vacuum. Prepared in this way, it is free from fat, leaves less than 0·5 per cent. of ash and contains 15·5 to 18 per cent. of nitrogen. From ordinary casein a modification known as *paracasein*, containing 14·8 to 15 per cent. of nitrogen, may apparently be separated. Commercial casein (*see* p. 385) contains less than 3 per cent. of ash and less than 0·1 per cent. of fat, and costs 64*s*. to 80*s*. per quintal. Riegel (Ger. Pat. 117,979 of 1900) precipitates it in a highly pure state from milk by means of ethylsulphuric acid. Casein is detected on textiles or paper by Adamkiewicz's reaction, a drop of a mixture of glyoxylic and sulphuric acids being placed on the surface, which is then gently heated over a flame: in presence of casein, the drop of liquid assumes a transitory violet-red colour.

(4) **PROTEINS WHICH COAGULATE (Fibrinogen, Myosin, &c.)** are distinguished by exhibiting a first coagulation under the influence of certain enzymes and a further coagulation by heat or absolute alcohol.

(5) **HISTONES (Globin, Nucleo-histone, &c.)** contain sulphur and are markedly basic in character; they are precipitated by alkalis, and in acid solution give insoluble compounds with the albumins. *Nucleo-histones* are obtained from the leucocytes of the thymus gland and from the testes of certain fish. The protein part of the hæmoglobin molecule of the red blood corpuscles consists of a histone, *globin*. The histones have certain properties in common with the peptones and albumoses.

(6) **PROTAMINES (Salmin, Clupein, Sturin, &c.)** do not contain sulphur but contain up to 25 per cent. of nitrogen and are composed mainly of diamino-acids (arginine); they are obtained from the spermatazoa of many fishes (salmon, herring, sturgeon, &c.). They and the histones are the least complex proteins.

They are still more basic in character than the histones and readily form platinichlorides, sulphates, and picrates, which are all crystalline. They are precipitated by dilute alkalis.

II. MODIFIED PROTEINS

(1) **ALBUMOSES and PEPTONES** are derived from true proteins by various transformations. The albumoses are soluble and cannot be coagulated, but are precipitable by ammonium sulphate and other salts. The peptones are regarded as the last decomposition products of the proteins which give protein reactions (the biuret reaction); on decomposition they give amino-acids without intermediate products.

(2) **SALTS OF PROTEINS (Syntonins or Acid-albumins, Albuminates)** are markedly acid in character.

III. CONJUGATED PROTEINS (PROTEIDS)

These represent combinations of proteins with other complex substances, and are coagulable by alcohol.

(1) **HÆMOGLOBIN** is the colouring-matter of red blood corpuscles and seems to be composed of a protein combined with a colouring-matter containing iron, as it can be decomposed into albumin and **Hæmatin**, $Fe(C_{16}H_{32}O_2N_2)_2$, the latter being a brown

substance containing 8 per cent. of iron. The hæmoglobin of venous blood is of considerable importance in respiration, as it combines very readily with atmospheric oxygen (when the blood traverses the lungs) forming **Oxyhæmoglobin**, which is found in arterial blood and carries the oxygen to the tissues, afterwards returning to the veins. With acetic acid and sodium chloride it gives *hæmatin hydrochloride* (*hæmin*) in characteristic, microscopic crystals in the form of reddish brown needles. **Blood-spots** (even old ones) may be detected by Teichmann's test: to a solution of the spot in a little glacial acetic acid are added a trace of sodium chloride and then a small quantity of pure concentrated acetic acid, the liquid being heated to boiling on a watch-glass and one or two drops of the hot solution placed on a microscope slide and allowed to evaporate slowly in the cold ; a drop of water is added, a cover-glass applied, and the slide observed under the microscope. The brown hæmin crystals resemble barley-corns, but are sometimes rhombohedral and generally crossed in groups (Fig. 506) ; viewed in polarised light between crossed nicols, they appear luminous and golden on a dark ground. They are insoluble in water or cold acetic acid, but dissolve in alkali.

Blood-stains may also be identified by means of the catalytic action of the hæmoglobin, which colours alcoholic guaiacol tincture or alkaline phenolphthalein previously decolorised by zinc-dust or, better, the leuco-base of malachite green (F. Michel, 1911).[1]

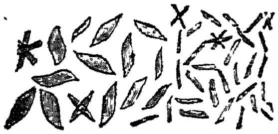


FIG. 506.—Hæmin crystals at different magnifications.

T. Gigli (1910) states that a very sensitive reaction is given by a fresh mixture of 3 drops of benzidine (5 per cent. solution in acetic acid) and 2 drops of 3 per cent. hydrogen peroxide solution ; a blue coloration is given immediately by a trace of blood. Bardach and Silberstein (1910) propose the use of guaiacum resin and sodium perborate.

Oxyhæmoglobin has a composition differing little from that of the proteins, but it contains 0·4 per cent. of iron combined in the ferric state, as with hæmin and hæmatin, whilst the reduction product of the latter, *i.e.* hæmoglobin, is a ferrous compound (W. Küster, 1910). In a vacuum (or under the action of ammonium sulphide) it loses oxygen, giving hæmoglobin.

Hæmoglobin forms a red crystalline powder soluble in water and reprecipitable in the crystalline state by alcohol. Both hæmoglobin and oxyhæmoglobin give characteristic absorption spectra.

Hæmoglobin and also its ash exert a catalytic action in certain combustion phenomena ; *e.g.* sugar moistened with a little human blood burns with great energy.

When a current of carbonic oxide is passed into a solution of red oxyhæmoglobin (defibrinated blood) the oxygen is displaced and the liquid assumes a violet-red colour, *carboxyhæmoglobin*—which can be obtained in bluish crystals—being formed. An aqueous solution of this compound (blood poisoned with carbonic oxide) gives two characteristic absorption bands between the D and E lines of the spectrum, and these bands do not unite or disappear—as happens in the case of oxyhæmoglobin—when a few drops of ammonium sulphide are added to the solution. Hæmoglobin itself gives a single absorption band between the D and E lines.

(2) **NUCLEOPROTEINS** or **Nucleins** have a pronounced acid character and are insoluble in water and acids, but soluble in alkali. They represent compounds of proteins

[1] Blood-spots may also be detected by means of hydrogen peroxide: it is sometimes sufficient to press a piece of moistened filter-paper on the dry blood-spot and then to immerse it in hydrogen peroxide solution, to obtain a copious evolution of oxygen.

To ascertain from what animal the blood comes, and in general to discover if it is human blood, Uhlenhuth's test (1909), based on the formation of different antitoxins in different animals (*see* p 115) serves. Tristovitch and Bordet (1899) showed, indeed, that if an extraneous serum (*e.g.* human) is injected in several doses into the blood of an animal (*e.g.* a guinea-pig), the serum of this animal (*antiserum*) ultimately acquires the property of precipitating (or rendering turbid in the case of dilute serum or dilute blood) the blood of the animal which furnished the injected serum (*e.g.* man). If even a very dilute solution of blood (obtained, for instance, by extracting a dried blood-spot with a little water) is cleared by filtration and treated separately with different clear antiserums to ascertain with which of them a turbidity is produced, it can be stated with certainty that the blood-spot was derived from the animal whose serum, when injected into the guinea-pig, produced the antiserum rendering the blood solution turbid. The test must be applied very carefully and with parallel control experiments; it does not distinguish between the bloods of similar animals, *e.g.* hens and pigeons, sheep and goats, apes and men. The difference between various species becomes more evident when dilute solutions or, better, dilute blood and a little concentrated antiserum are employed. All these phenomena, studied by Uhlenhuth, and subsequently by others, are based on the precipitation of the albuminoid substances of the different serums (*precipitins*), and they allow of the determination of the character of blood-spots sixty years old. Clear solutions and sterilised vessels are always used for the test.

with a **Nucleic Acid,** which is phosphoric acid neutralised partially by basic organic groups, such as xanthine, guanine, &c. The nucleins contain 5·7 per cent. P, 41 per cent. C, and 31 per cent. O, and are hence sharply distinguished from true proteins although they give the same colour reactions. They form the fundamental constituents of cell nuclei.

(3) **GLUCOPROTEINS** are acid in character and are formed of a protein combined with a sugar derivative. They are insoluble in water and with a little lime-water give neutral, frothy, and ropy solutions which are not coagulated by heat or by nitric acid. When hydrolysed with alkali or acid they yield sugar, peptones, and **Syntonins.**

These compounds, which are poor in nitrogen (11·7 to 12·3 per cent.), include the **Mucins.**

IV. ALBUMINOIDS

These constitute the fundamental parts of the cartilaginous tissues and epidermis of animals and comprise:

(1) **ELASTIN,** which forms the elastic part of the tendons and ligaments, is insoluble in dilute acid or alkali, but with the latter loses the whole of its sulphur.

(2) **KERATIN** is the principal constituent of the nails, horns, feathers, epidermis, hair, &c. It is insoluble in water, but when heated under pressure, best in presence of alkali, it dissolves with partial decomposition. It contains 4·5 per cent. of sulphur, which is eliminated to some extent by boiling water.

With nitric acid it gives the yellow xanthoprotein reaction (*see above*, Blood-spots on skin treated with nitric acid).

(3) The **COLLAGENS** are abundant in bones, hair, tendons, and cartilage. They combine with water at the boiling-point and dissolve, forming ordinary *glue* or *gelatine*, which is precipitated by tannin or by mercuric chloride acidified with HCl but not by mineral acids. They contain stably combined sulphur. They consist, to the extent of 85 per cent., of amino-acids (Skraup, Biehler and Böttcher, 1909–1910), and, like the protamines, are true proteins containing methoxy- and azomethyl-groups. Unlike casein, they give little glutamic acid on hydrolysis. On hydrolysing them with caustic baryta, E. Fischer and R. Boehner (1910) obtained **Proline** (*α-pyrrolidinecarboxylic acid*) as primary product; **α-Amino-δ-hydroxyvaleric Acid,** which is obtained from gelatine, does not give proline with baryta. By digesting gelatine with trypsin, Levene (1910) obtained mainly **Prolylglycocoll Anhydride.** The absorptive power of the collagens for carbon disulphide, which in presence of alkali leads to thiohydration, allows of their differentiation from agglutinating substances (Sadikow, 1910); the agglutination of gelatine is not only a disgregation of the collagen molecule, but also a condensation of the side-chains. Gelatine which has undergone prolonged exposure to light loses some of its absorptive power for water owing to the formation of formaldehyde, which hardens the glue (Meisling, 1909). On hydrolytic decomposition, the collagens give glycocoll (while the albumins give tyrosine), leucine, glutamic acid, and asparagine.[1] Very dilute solutions of glue give, with boiling ammonium molybdate solutions, a characteristic precipitate and coloured solution, which may be applied to quantitative estimations (E. Schmidt, 1910).

[1] **Manufacture of Glue and Gelatine.** The prime materials are bones and hide waste, generally untanned and preserved with lime. From bones the fat is first extracted (*see* p. 392 and also vol. i, p. 508), and the crushed bones then heated for a couple of hours in a large autoclave with water and steam under pressure, so as to convert the *ossein* into soluble gelatine; this treatment is repeated two or three times, the final more dilute solutions being used for a subsequent operation. In some cases, however, the bones and hence also the glue are freed from calcium phosphate by treatment with four times their weight of 6 to 7 per cent. hydrochloric acid (sp. gr. 1 05) until complete softening occurs; the calcium phosphate is precipitated from the solution by means of lime and calcium carbonate, while the ossein, placed in a double-bottomed vessel heated by steam, is rapidly converted into a solution of glue. According to Ger. Pat. 144,398, the calcium phosphate may be dissolved by aqueous SO_2 *under pressure* (only the treatment under pressure is patented). The solution obtained by either of these methods, with a concentration of 17° to 18° on the glue-densimeter in summer and 12° to 14° in winter, can be partly decolorised, while still hot, by a current of sulphur dioxide; it is then introduced into zinc moulds surrounded by cold water to solidify. The solidification of these solutions (and even more dilute ones) is now hastened by refrigeration The solid blocks of glue are then cut into suitable sizes and dried on wide-meshed nets arranged on trolleys, which are placed in chambers through which air at 25° to 30° is circulated by means of fans. If the air is above this temperature the glue will melt, while if it is too dry the cakes are deformed. On this account and also because it would readily putrefy, glue is not made in summer. Dry *bone-glue* contains 15 to 20 per cent. of water and costs 52*s.* to 68*s.* per quintal.

Skin-glue (leather glue) is prepared from hide-waste and also other waste (nerves, cartilage, &c.) by defatting with carbon disulphide and softening or swelling in water, which likewise removes impurities. It is then macerated for three weeks in a series of vessels containing milk of lime, which is frequently renewed to eliminate any remaining fat, blood, &c. It is then thoroughly washed in water and the last traces of lime (which would make the glue turbid) removed by means of dilute hydrochloric acid, or, better, of sulphur dioxide or phosphoric acid. The

V. VARIOUS PROTEINS

Spongin enters into the formation of sponges; its hydrolytic products approximate more to those of the collagens than to those of the albumins, but they are more resistant to the action of soda and baryta than collagens. **Cornein** constitutes coral and gives leucine on hydrolysis. **Fibroin** and **Sericin** are obtained from silk (*see* p. 692); fibroin dissolves in energetic alkalis with elimination of ammonia and formation of **Sericoin**, and when completely hydrolysed it yields tyrosine and glycocoll but not leucine.

The **Enzymes** (*see* p. 111) belong to the group of complex albumins.

GLUCOSIDES AND OTHER SUBSTANCES OF UNCERTAIN OR UNKNOWN COMPOSITION

Glucosides have been defined and the synthesis of artificial glucosides described on pp. 432 and 437. They are compounds of aromatic or aliphatic compounds with carbohydrates. In vegetable organisms these glucosides form, according to Pfeffer, difficultly dialysable substances which serve the plants as reserve material, gradually becoming utilisable as they are decomposed by the various enzymes occurring in other cells. This was well shown by T. Weevers (1903 and 1908) for **Salicin**, which is decomposed (by emulsin) into glucose and saligenin (hydroxybenzyl alcohol), the latter being probably further transformed into a final product known as **Catechol**. The latter is a phenol found throughout the whole plant (*e.g. Salix purpurea*), and its quantity is inversely proportional to that of the salicin present; it is possible that it reacts with fresh quantities of glucose regenerating salicin. While the sugars are gradually utilised in the growth of the plant, the aromatic group (which serves as a reserve of carbon for bacteria but not for enzymes) is used in the continuous reconstruction of the glucoside. So that plants are able to prepare reserve materials in different ways: when the carbohydrates are not utilised, they are transformed into insoluble starch, or into glycogen, or into glucosides.

AMYGDALIN, already mentioned on p. 113, has a composition corresponding with $C_{20}H_{27}O_{11}N$ and forms colourless crystals which are soluble in water and melt at 200°.

waste prepared in this way is treated with hot water and steam in wooden vessels with false bottoms and the first solutions, showing densities of 16° to 20° on the glue-densimeter, are solidified in moulds as above. The two or three succeeding extracts, which are more dilute, are concentrated to 20° to 22° in a single or multiple-effect vacuum apparatus (*see* p. 461), surmounted by a column with perforated discs to break up the froth, and are then allowed to set. Good results are now obtained with Kestner concentrators (*see* vol. i, p. 443). The waste used gives about one-third of its weight of dry glue, which is sold at 96*s*. to 128*s*. per quintal. The finer qualities, filtered, decolorised, and prepared from pure, fresh, raw materials, bear the name of *gelatine* and cost £6 to £12 per quintal.

In order to utilise tanned hides in the manufacture of glue it is necessary to untan them by successive treatment with dilute alkali solution, water, and lime; if chrome tanned, they are treated first with dilute sulphuric acid, then with an abundant supply of water and finally with lime. In either case, the remaining traces of lime are removed by means of dilute HCl, the latter being eliminated by treatment with alkali and washing with water (Eng. Pat. 22,738 of 1902).

Fish-glue is obtained from the well-purified swimming-bladders of various species of *Acipenser*, especially of *Acipenser sturio* (sturgeon), by treatment with acid, lime, steam, water, &c. According to Ger. Pat. 131,315, the blubber of whales may also be used. Fish-glue costs double or treble as much as the best qualities of other glue.

Liquid glue is obtained by the protracted heating of glue with its own weight of water and one-fourth or one-third of its weight of hydrochloric, acetic, or nitric acid (the last at 35° Bé; the nitrous fumes must be carried away by a good draught). F. Supf (Ger. Pat. 212,346 of 1908) obtains liquid glue by treating, say, 450 kilos of glue with 120 kilos of sodium naphthalenesulphonate.

Glue is *analysed* by determining the ash (2 to 3 per cent.) and the increase in weight caused by immersion for 12 hours in cold water (in which it should not dissolve), the best qualities absorbing most water and swelling. The ash of bone-glue has an almost neutral reaction, and chlorides and phosphates are found in its nitric acid solution. The ash of hide-glue does not melt, has an alkaline reaction, and contains little or no phosphoric acid. The aqueous solution of pure glue has a neutral or very faintly acid reaction, while those of the more impure kinds are sometimes alkaline. Glue should be completely soluble in hot water, any undissolved part representing impurity. The moisture content of dry glue should not exceed 15 to 18 per cent (lost at 105°). The best qualities melt at the highest temperatures and the dropping-point may be determined by Ubbelohde's apparatus (*see* p. 6), using a larger vessel. The relative adhesive powers of different glues may be estimated by preparing tepid solutions of equal concentrations, immersing pieces of cotton or woollen fabric (of equal weights and areas) in them for two or three minutes, centrifuging the fabrics at the same time in the same centrifuge, ironing them slightly with a hot iron, drying completely in an oven at 100° and then noting which of the fabrics adheres best and longest to the fingers.

Statistics. Italy has a protective duty of 38*d*. per quintal on glue and 12*s*. per quintal on fish-glue. In 1904 the exports were 11,000 quintals of glue (11,700 in 1902) and the imports 10,600 (more than one-half from Austria), besides 800 quintals of gelatine and 41 of fish-glue. The industry in Italy is injured by the competition of the Austrians, who have a protective duty of 8*s*. per quintal on glue and purchase nearly all the bones in Italy (16,600 quintals in 1903; 29,400 in 1904; 50,000 in 1905). Austria competes also with Germany.

In 1905 Germany exported 63,300 quintals of glue and gelatine at an average price of 52*s*. per quintal and imported 45,000 quintals at 44*s*. per quintal.

It is found in the stones of various fruits (cherries, peaches, bitter almonds, &c.) and in the leaves of the cherry-laurel. When hydrolysed by acids or enzymes (*see* pp. 111 and 112), it yields dextrose, prussic acid, and benzaldehyde.

SAPONIN, $C_{32}H_{52}O_{17}$, is obtained from Saponaria root, quilaya bark, and the Indian chestnut. It is used for washing garments in place of soap, and is also employed to produce a persistent froth (*e.g.* to give a head to beer). It is soluble in water, has an irritating taste and smell, and dissolves red blood corpuscles (is hence poisonous). It is extracted in various ways according to Ger. Pats. 116,591, 144,760, and 156,954. The crude product costs 9*s.* 6*d.* per kilo ; the purified, 20*s.*, and the puriss., 40*s.*

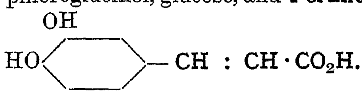
DIGITALIN, $C_{35}H_{56}O_{14}$ (?) ; DIGITONIN, $C_{27}H_{46}O_{14}$, and DIGITOXIN, $C_{31}H_{54}O_{11}$, are the most important constituents of the foxglove (*Digitalis purpurea*) and are used in medicine, especially for diseases of the heart. Pure digitalin costs 10*d.* per gramme, and crystallised digitoxin 20*s.* per gramme.

SALICIN, $C_{13}H_{18}O_7$ (*see* p. 574), is contained in several varieties of Salix, and on hydrolysis gives glucose and saligenin (*see* pp. 574, 582) ; with nitrous acid it forms **Helicin**, $C_{13}H_{16}O_7 + H_2O$, which can also be obtained synthetically from glucose and salicylic aldehyde.

ÆSCULIN, $C_{15}H_{16}O_9$, is obtained from horse-chestnut bark, and is the glucoside of ÆSCULETIN (a Dihydroxycoumarin), $C_6H_2(OH)_2\left\langle\begin{array}{l}CH:CH\\ \quad\;\; | \\ O-CO\end{array}\right.$, which is isomeric with *daphnetin.*

POPULIN, $C_{20}H_{22}O_8 + 2H_2O$, is a **Benzoylsalicin**, and is obtained synthetically from salicin and benzoyl chloride ; it occurs naturally in *Populus.*

HESPERIDIN, $C_{22}H_{26}O_{12}$, occurs abundantly in the bitter orange, and on decomposition gives phloroglucinol, glucose, and **Ferulic Acid**, which is the monomethyl ether of

Caffeic Acid, 

PHLORETIN, $C_{15}H_{14}O_5$, and its glucoside, PHLORIDZIN, $C_{21}H_{24}O_{10}$, are found in plants, and in cases of glycosuria in animals.

IRIDIN, $C_{24}H_{26}O_{13}$, is found in the roots of the Florentine iris and yields **Irigenin** and glucose on hydrolysis.

ARBUTIN, $C_{12}H_{16}O_7$, occurs in the leaves of the bear-berry and gives glucose and hydroquinone on hydrolysis. **Methylarbutin** gives glucose and methylhydroquinone.

CONIFERIN, $C_{16}H_{22}O_8 + 2H_2O$, is hydrolysed to glucose and **Coniferyl Alcohol**, which gives *vanillin* on oxidation. It is found in the sap of *Coniferæ.*

SINIGRIN (Myronic Acid), $C_{10}H_{17}O_9NS_2$; hydrolysis of its potassium salt, which occurs in black mustard seed, gives glucose, potassium bisulphate, and allyl mustard oil.

SANTONIN, $C_{15}H_{18}O_3$; its constitution has been studied more especially by Cannizzaro and his pupils. It is a naphthalene derivative and is found in worm-seed (santonica).

ALOIN, $C_{17}H_{18}O_7$, an anthracene derivative, occurs in aloes and is a strong purgative.

LECITHIN (composition, *see* p. 374) is a characteristic component of egg-yolk and of brain and nerve matter and is a crystalline waxy substance, which dissolves in alcohol or ether and with water forms an opalescent liquid. When hydrolysed it yields glycerophosphoric, oleic, and palmitic acids, together with choline, and it may therefore be regarded as a glyceride (*see* pp. 183, 372).

Considerable use has been made of it (and also of bromo- and iodo-lecithin) in recent years as a medicine. Lecithin is extracted on the large scale from egg-yolk, and new processes are described in Fr. Pats. 371,391 and 406,634 of 1908. Pure lecithin costs up to £8 per kilo.

CEREBRIN, $C_{17}H_{33}O_3N$, occurs in the nerves.

IODOTHYRIN (*see* vol. i, p. 151) is the iodine compound of the thyroid gland.

Bile Compounds include TAUROCHOLIC ACID, $C_{26}H_{45}O_7NS$, and GLYCOCHOLIC ACID, $C_{26}H_{43}O_6N$, as sodium salts. When decomposed by alkali, both acids yield **Cholic Acid**, $OH\cdot C_{21}H_{32}(CH_2\cdot OH)_2(CO_2H)$, glycine and taurine. Bile also contains colouring-matters such as BILIVERDIN, BILIFUCHSIN, and BILIRUBIN, $C_{16}H_{18}O_4N_2$.

CANTHARIDIN, $C_{10}H_{12}O_4$, occurring in cantharides, causes blistering of the skin, and sublimes in thin scales.

CHITIN forms the skeletal matter of crustaceans. It is insoluble in alkali (unlike keratin) and when hydrolysed by acid gives a glucosamine. Fusion with potash at 184° yields acetic acid and **Chitosan**, which also forms the glucosamine with acid.

CHOLESTEROL, $C_{27}H_{46}O$, occurs in many plants and animals (that of plants is called **Phytosterol**), generally together with fats and oils; certain physical differences but virtually no differences in chemical behaviour are observable in products of different origin. Its constitution has not been definitely established, but, owing more especially to the investigations of A. Windaus, many of its component groups have been ascertained. A doubt whether the complex contained one or two double linkings formerly existed, but the addition of ozone (Molinari and Fenaroli, 1908) shows the presence of two such linkings in both phytosterols and other cholesterols.

It forms shining scales melting at 147°, and in constitution it resembles the terpenes more than the substances of any other group, but in all probability it does not contain benzene groups. Minimal quantities of cholesterol may be detected by Tschugajew's reaction, which consists in the formation of a more or less intense red coloration when a small quantity of a substance containing cholesterol is poured into fused anhydrous trichloroacetic acid. In alcoholic solution, cholesterol and phytosterol (but not their ethers) form an insoluble compound with **Digitonin**; this reaction serves for the estimation of these substances and for their separation from other animal and vegetable organic compounds, such as hydrocarbons, &c.

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